INVESTIGATION OF THE MINERALOGICAL CHARACTERISTICS OF FINE PARTICLE RESIDUES

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MINERALOGICAL CHARACTERISTICS OF FINE PARTICLE RESIDUES

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ABSTRACT

Solid residues are generated at various stages of metal production. Some of these residues still contain significant quantities of metals. In determining possible process routes for residues a detailed knowledge of the mineralogy (i.e. the minerals or phases present) is required. This thesis examines the mineralogical characteristics of four residues: copper smelter dust, jarosite residue and hot-acid-leach residue all from the metallurgical plant of Kidd Creek Mines Ltd., and low-acid-leach residue from the Canadian Electrolytic Zinc plant.

The methodology of characterization included the fractionation of the residues based on particle size, magnetic susceptibility and leach ability in sulphuric acid. The fractions were analysed by X-ray diffractometry and electron beam techniques.

A major phase in all the residues was zinc ferrite. The characterization of this phase showed that it does not have the stoichiometric composition of $ZnFe_2O_4$ but exhibits a variable composition of the type $Zn_xFe_{3-x}O_4$. This variable composition corresponds to a measured variation in magnetic susceptibility of the ferrites.

Some treatment routes for these residues are examined; special emphasis was placed on the potential application of magnetic separation. The hot-acid-leach residue appeared the most amenable to magnetic separation.

RÉSUMÉ

Les différentes étapes de production des métaux engendrent des résidus solides. Certains de ces résidus contiennent encore des valeurs intéressantes de métal. Afin de trouver des procédés pour traiter ces résidus l'on se doit d'en connaître la minéralogie exacte (i.e. les minéraux ou phases présents). Cette thèse porte sur l'étude détaillée des caractéristiques minéralogiques de quatre résidus: des poussières de fonderie de cuivre, des résidus de jarosite et de lixiviation à l'acide chaud, tous trois provenant des installations métallurgiques de Kidd Creek Mines Ltd., et un résidu de lixiviation à l'acide à basse concentration provenant de l'usine de Canadian Electrolytic Zinc.

Pour caractériser les résidus, la méthodologie consiste à fractioner les résidus par: distribution granulométrique, susceptibilité magnétique et lixiviation à l'acide sulfurique. Les fractions obtenues furent analysées à la diffraction X et au microscope à balayage électronique.

La phase majeur de tous ces résidus fut la ferrite de zinc. En caractérisant cette phase, il nous est apparu que cette dernière ne démontre pas la composition stoechiométrique $ZnFe_2O_4$ mais plutôt une composition variable de type $Zn_zFe_{3-z}O_4$. On a pu établir un lien entre cette composition variable et la variation de susceptibilité magnétique des ferrites.

On y propose aussi certaines routes pur traiter ces résidus, examinant particulièrement le potentiel d'une séparation magnétique. Les résidus de lixiviation à l'acide chaud semblent être ceux offrant le meilleur potentiel pour une séparation magnétique.

RESUMEN

En diferentes etapas de la producción de metales, se pueden generar varios residuos sólidos; algunos de éstos todavía contienen cantidades significativas de metales. Para poder determinar los métodos de procesado de dichos residuos, es necesario tener información detallada de su mineralogía, es decir establecer cuales minerales o fases están presentes. Esta tesis examina las características mineralógicas de cuatro residuos metalúrgicos: polvos de fundición cobriza, precipitado de jarosita, residuo de la lixiviación en caliente con ácido sulfúrico, y residuo de la lixiviación con concentraciones bajas de ácido. Los tres primeros de la planta metalúrgica de Kidd Creek Mines Ltd., y el último de la planta Canadian Electrolytic Zinc.

La metodología de la caracterización incluyó el fraccionado de los residuos con respecto al tamaño de particula, susceptibilidad magnética y solubilidad en ácido sulfúrico. Todas las fracciones fueron estudiadas haciendo uso de diferentes técnicas, pero principalmente mediante difracción de rayos-X y microscopía electrónica. La información recopilada de todas las fracciones fué integrada para obtener la caracterización más completa de cada residuo original.

Entre los hallazgos de ésta tesis, se encontró que la ferrita de zinc es una fase importante en todos los residuos estudiados. Su importancia radica en que representa pérdidas de zinc y es la fase más resistente a solubilización en ácido sulfúrico. La caracterización de esta fase mostró que no tiene una composición estoquiométrica fija (ZnFe₂O₄), sino que exhibe una composición variable del tipo Zn_zFe_{3-z}O₄. Se encontró que ésta variación en composición esta relacionada con los valores medidos de la susceptibilidad magnética de la ferrita.

La presente tesis trata principalmente sobre la caracterización de los mencionados residuos. No obstante algunos posibles tratamientos son examinados, con especial énfasis en el potencial de aplicación de la separación magnética. De los residuos estudiados, el de la lixiviación ácida en caliente mostró buenos resultados al ser tratado por separación magnética.

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Last, but never least, my special thanks to Loyda, my wife, for enduring all the years of my life as graduate student. She, more than anyone, knows what it took.

THESIS STRUCTURE

This thesis uses the option of including as part of the text five original papers published in learned journals.

The thesis is structured in four sections:

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- 1. An extended introduction to the investigation including a review of the literature on characterization of metallurgical residues.
- 2. A description of the experimental techniques.
- 3. A section including the five published manuscripts with connecting text.
- 4. A section containing the Summary of findings and Discussion, the Conclusions, and the Claims for original contributions.

In general the five manuscripts can be read as chapters without breaking the text structure.

Three appendices are attached at the end of Manuscript V to augment the information.

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STATEMENT ON CONTRIBUTION OF THE AUTHOR AND CO-AUTHORS

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Manuscript I:

Mr. R. Lastra should be credited for all the experimental work. Including sample preparation for EM observations, all the SEM and STEM studies, and all the X-ray diffraction tasks. Credit is also claimed for the analysis of results. Dr. Neil Rowlands should be credited for help in writing the manuscript.

Manuscript II:

The author should be credited for all the work contributing to the mineralogical analysis including X-ray fluorescence, X-ray diffractometry, thermodynamic predictions, sample preparation for EM observations, SEM and STEM studies, EDS analysis, and preparation of the original manuscript. Dr. S. R. Rao should be credited for the Atomic Absortion analysis, the particle size analysis, the sulfuric acid leaching and for the magnetic separation work. The author thanks his supervisors Dr. N. Rowlands and Dr. J. A. Finch for the English corrections during writing of the manuscript and their advice on the presentation of the results and discussion.

Manuscripts III and IV:

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The author should be credited for all the work contributing to the mineralogical analysis including X-ray flourescence, X-ray diffractometry, sample preparation for EM observations, SEM and STEM studies, EDS analysis, and preparation of the original manuscript. Dr. S. R. Rao should be credited for all the sulfuric acid leaching and for the magnetic separation work. The author thanks his supervisors Dr. N. Rowlands and Dr. J. A. Finch for the English corrections during writing of the manuscript and their advice on the presentation of the results and discussion.

Manuscript V:

The author should be credited for all the experimental work including gasnull pycnometer measurements, particle size analysis, magnetic separation, X-ray diffractometry, sample preparation for SEM observations, and particle characterization by EDS and image analysis, and the preparation of the original manuscript. The author thanks his supervisors Dr. N. Rowlands and Dr. J. A. Finch for the English corrections during writing of the manuscript and their advice on the presentation of the results and discussion.

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SECTION I

INTRODUCTION

I.1 METALLURGICAL RESIDUES

Metallurgical residues include slags associated with ferrous and non-ferrous smelting, fine-grained particulates such as precipitator dusts from stacks, and finely disseminated waste products from electrolytic and other hydrometallurgical processes. These products are important not only because they may be environmentally hazardous if dumped, but also because they represent a loss since they often contain metal values in concentrations higher than those in the original ores. Two such examples are the dusts from copper smelting and from iron and steelmaking. Typical assays of these two residues are given in Table I.1.

Table I.2 [147] lists the pollutants regulated (1980) by the U.S. Environmental Protection Agency. Comparison of Tables I.1 and I.2, clearly shows that the dusts from these operations represent an environmental hazard if simply dumped. This is specially true if the residues contain environmentally-leachable phases of As, Pb, Cd, and Se.

In addition to environmental hazards, dumping of residues represents a potential loss of metal values. The metal value of the residues is well illustrated with the case of dusts from the steelmaking industry: the zinc content in these dusts in the US, is equal to about 10% of that country's imported zinc requirements [81, 82].

The environmental problems related to the solid wastes from smelters and refineries, and the associated metal value losses have increased the interest in further treatment of these residues.

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Table I.3 gives a summary of the published research directly related to the treatment of dust residues. Table I.3 was created using the information provided by a computer bibliographical search (DIALOG) through the following databases: Metadex 1966-1984; Compendex 1970-1984 and Chezuical Abstract 1967-1984. Table I.3 quotes 100 references related to dust treatment. Even though Table I.3 is not intended to be a complete list of the related references, it shows the significant effort directed to the treatment of dusts. On the other hand, the literature on the mineralogical characterisation of the residues is less abundant. However, it is generally accepted that mineralogical characterization of the residues is important. The clearer understanding of their constituents obtained from mineralogical examination, for example, will help in selecting the form of treatment.

From the foregoing, the growing interest in residue characterization is understandable. Goldstein et al, [81] have performed research on the characterization of electric furnace dusts. Dutrizac and co-workers have characterized several residues from non-ferrous processes, [94, 96, 97, 120]. The work in this thesis deals with the characterization of four residues: Smelter dust from the Mitsubishi-copper plant of Kidd Creek (Reported in Manuscript II); Jarosite residue and Hot-acid-leach residue (HAL) from the hydrometallurgical zinc plant of Kidd Creek (Manuscripts III and IV) and low-acid-leach residue of the Canadian Electrolytic Zinc (CEZ) plant (Manuscript V).

$ \begin{bmatrix} \% \end{bmatrix} & CS^{*2} & SS \\ [\%] & [\%] & [\%] & [\%] \\ Cu & 10-49 & 0.17 & 1. \\ Fe & 5-43 & 35.4 & 33 \\ Zn & 8-23 & 18.75 & 1. \\ STOTAL & \approx 11 & 0.33 & 0. \\ Pb & 7-26 & 1.47 & 1. \\ As & 0.9-1.8 & *5 & * \\ Sn & \approx 1.4 & 0.025 & 0. \\ Cd & \approx 0.6 & 0.02 & 0. \\ Si & 0.1-0.9 & 2.41 & 3. \\ Na & \approx 0.05 & 0.60 & 0. \\ Ya & \approx 0.12 & 1.00 & 1 \\ \end{bmatrix} $	5-3 76 1.2 17 26 12 5 01 17
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	53
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Sb <0.02 ···· ·	••
Ag (ppm) 200-550 *5 *	5
In trace *4	••
T1 trace *4	••
Se trace *4 *5 *	'5
Ni trace *4 0.03 1.	96
Co trace *4 0.01 0.	03
Bi trace *4 *5 *	5
Cr 0.64 10	.70
Mn 3.50 6.	70
Mo 0.03 0.	35
V <0.1 <	0.1
Li ··· <0.1 <	0.1
Ca 3.73 2.	48
Mg 1.50 2.	22
CI 1.27 0.	40
AI 0.34 0.	38
F 0.92 2.	98
C 0.45 0.	

Table I.1	. Typical	l assay c	of copper	smelting	and	steelmaki	ng d	usts.
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notes:

notes: 1 Cottrell dust from the Kidd Creek plant (Mitsubishi process) [94, 145]. 2 Composite dust from carbon steelmaking. [144] 3 Composite dust from stainless steelmaking [144] 4 Inferred to be present from analysis of leaching solutions. 5 Known to be present in variable concentrations [146] ... Data not known

Table I.2. Metal mining and processing sources regulated by effluent guidelines and standards [147]

Category/Ref	Subcategory	Pollutants Regulated
Iron and steel	By-product coke	NH ₃ , CN ⁻ , oil and grease
manufacturing	Beehive coke	phenol, TSS, pH
40CFR420	Sintering	Oil and grease, TSS, S ⁻ , F ⁻ , pH
	Blast furnace	TSS, CN ⁻ , phenol, NH ₃ , S ⁻ , F ⁻ , pH
	Open hearth f.	TSS, F^- , NO_5^- , Zn , pH
	Basic oxygen f.	TSS, F ⁻ , pH
	Electric arc f.	TSS, F ⁻ , Zn, pH, Pb, Cd, Cr
	Vacuum degassing	TSS, Zn, Mn, Pb, NO ₃ , pH
Nonferrous	Bauxite refining	
metals/	Primary aluminium	TSS, F ⁻ , pH
40CFR421	smelting.	
	Secondary aluminum	
	smelting.	TSS, F ⁻ , NH ₃ , Al, Cu, COD, pH
	Primary copper	
	smelting.	TSS, As, Cu, Pb, Cd, Se, Zn, pH
	Primary copper	TSS, As, Cu, Se, Zn, oil and
	refining.	grease, pH
	Secondary copper	TSS, Cu, Zn, oil and grease, pH
	Primary lead	TSS, Cd, Pb, Zn, pH
	Primary zinc	TSS, As, Cd, Se, Zn, pH
Ferroalloy	Electric furnaces	TSS, Cr, Mn, pH
manufacturing/	Other smelting	TSS, Cr, Mn, CN ⁻ , phenol, pH
40CFR424	Slag processing	TSS, Cr, Mn, pH
	Calcium carbide	
	furnaces.	TSS, CN ⁻ , pH
	Electrolytic	
	manganese.	TSS, Mn, NH ₃ , pH
	Electrolytic	
	chromium.	TSS, Mn, Cr, NH ₃ , pH
Ore mining and	Iron ore	TSS, Fe, pH
dressing/	Base and precious	
40CFR440	metals.	TSS, Cu, Zn, Pb, Hg, Cd, pH
	Aluminium ore	TSS, Fe, Al, pH
	Ferroalloy ores	TSS, Cd, Cu, Zn, Pb, As, pH
	Uranium, radium	
	and vanadium.	TSS, COD, As, An, Ra226, NH3, pH
	Mercury ore	TSS, Hg, Ni, pH
	Titanium ore	TSS, Fe, Zn, Ni, pH

Table I.3. Summary of references di	rectly related with the treatment of
dust residues. sources: Metad	ex (1966-1984); Compendex (1970-
1984) and Chemical Abstract	s (1967-1984)

TYPE OF TREATMENT	TREATMENT FOR Cu-Zn RESIDUES	TREATMENT FOR Pb RESIDUES	TREATMENT FOR Steel and Foundry	TREATMENT FOR OTHER RESIDUES
HYDROMETALLURGICAL (H2SO4-BASED)	1-23, 83, 86, 88-92	2, 8, 10, 19, 50-52, 86	68-71	58-59
(OTHER SOLVENT)	20, 24-31 88, 89, 91, 93	28	72-93 160-164	29, 31, 60
PYROMETALLURGICAL	3, 8, 9, 17, 32-37 86	36, 53-56, 86	69, 73-76 81, 82, 85	61-67
MIXED HYDRO-PYRO	5, 8, 9, 31, 38-43	57	69, 81	
FIXATION FOR DISPOSAL	16, 44-46			
FLOTATION-SMELTING	47			
SIZE-CLASIFICATION AND PYROMETALLURGICAL			77-80	
SIMULTANEOUS LEACHING AND FLOTATION	49			

I.2 ELECTRON MICROSCOPY

The mineralogical characterisation of residues is not easy since they tend to be multi-phase in composition and their constituent particles are very small, often 80% finer than 10 μ m. Elemental concentrations may be readily determined by atomic absorption (AA) or X- ray fluorescence spectrometry (XRF). However, determination of the phases present in the residues is much more complicated. Optical microscopy methods cannot be applied since little information can be gained from particles below about 20 μ m. The more direct route for phase identification is X-ray diffractometry (XRD). However this technique does not give phase associations for individual particles. Also, in many cases the residues are poorly crystalline. Because of their multi-phase nature and poor crystallinity, complex XRD spectra are produced that are difficult to interpret. The problem of phase identification can be eased by the use of electron microscopy.

Electron Microscopy (EM) techniques such as Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Electron Probe Microanalyzer (EPMA) and Scanning-Transmission Microscopy (STEM) have been applied in the characterization of a variety of residues [81, 94- 97, 120, 148]. All these techniques use an electron beam source which is converged, focused and moved (scanned) with the use of magnetic lenses. The general operating principle of this instruments can be understood by comparing the well known optical-transmitted light microscope (OM) and the TEM. Figure I.1 shows simplified schematic diagrams of these two microscopes. It can be seen that the "illuminating" source of the TEM is an electron beam, that of the OM is visible or ultraviolet light.

The electron microscope has a higher resolving power that the optical microscope. In general, a microscope can, at best permit discrimination of two point objects greater than 0.7 $\lambda \sin \theta$, where λ is the wavelength of the illuminating radiation, and θ is the aperture angle of the cone of radiation illuminating the particles. Figure I.2 illustrates, in a simplified way, the reason that the TEM has a greater resolution that the optical microscope.

Quotations of the maximum resolution for commercial TEM instruments varies between 0.14 nm to 0.34 nm (for 1250 kV to 100 kV of accelerating voltage of the electron beam).





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	VISIBLE LIGHT	ULTRAVIOLET LIGHT IN AN INMERSE MEDIUM OF REFRACTIVE INDEX 1.5
≈ λ	500nm	170nm
	350nm	119nm



 $\text{SIN}\, \Theta \texttt{=}\, 5 \times 10^{\cdot3}$

	ELECTRON BEAM ACCELERATING VOLTAGE		
Γ	20KV	100 KV	
≈ λ	0.0085nm	0.0037nm	
RESOLVING POWER	1.2nm	0.50nm	



Figure I.2. Schematic illustration of resolving power in the a) optical microscope and b) TEM [150]
A limitation of TEM is that the specimens must be very thin (≈ 0.1 to 0.8 μ m) to allow the transmission of the electron beam. In that respect the SEM has an advantage. It gives images through interaction with the surface of the specimen and, therefore, specimen thickness is not a restriction. Figure I.3 depicts these interactions. The SEM conventionally uses the secondary electrons to produce an image (SEI). However with suitable detectors all the other interaction signals can be used to produce images. Figure I.4 shows a schematic view of a SEM. The microscope has scanning coils to move the electron beam over the surface of the specimen. A detector that is sensitive to the chosen output signal from the specimen is connected through a video amplifier to the grid of a cathode ray tube that is scanned in synchronism with the beam on the specimen. In other words, the brightness at any point on the screen will depend on the strength of the signal from the corresponding point on the specimen. Besides the advantage of working with thick specimens, the SEM also provides a large depth of focus in secondary mode (SEI). However, the resolution of the SEM is lower than that of the TEM. Quotations of maximum resolution for commercial SEM instruments varies between 2.5 nm to 5 nm.



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Figure I.4. Schematic view of a SEM [151]. The details (for example, the number of lenses) vary between different manufacturers.

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Figure I.5 depicts the EMPA. From Figures I.4 and I.5 it can be seen that the SEM and the EMPA are very similar instruments. Elemental analysis can be performed using the characteristic X-rays resulting from the electron-specimen interactions (Figure I.3). The detection of X-rays can be done with wavelength dispersive systems (WDS) or with energy dispersive systems (EDS). The former exhibits a detection limit of ≈ 0.1 wt % compared to ≈ 0.5 wt % for EDS. However WDS systems only allow for detection of characteristic X-rays of one element per spectrometer. In contrast EDS systems allow simultaneous analysis over the elemental range sodium to uranium (the lower atomic number-element limit could be as low as boron, depending on the type of detector).

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It is possible to find combined commercial instruments such as the SEM-EMPA, the SEM-EDS-WDS, the EMPA-WDS-EDS, the SEM-Transmission (a SEM with a detector for transmitted electrons) and the STEM (a TEM with detectors for SEI or BEI, etc). Among these instruments, the STEM offers the possibility of performing scanning microscopy with better resolution (≈ 3 nm) than conventional SEM.

Further details on TEM, SEM, EMPA, STEM, EDS and WDS can be found in references [126, 128, 151-159].

Using electron microscopy techniques, the study of fine-particulate residues becomes possible. With EDS or WDS systems to detect X-Rays, the elemental composition of particles is determined, from which the phase(s) and the phase associations can be inferred. Crystallographic information for phase identification can be obtained by electron diffraction patterns in Transmission Electron Microscopy (TEM). Figure I.6 shows schematically the principle of the generation of electron diffraction patterns in TEM. Incident electron waves are scattered by atoms having regular three dimensional arrangements. The result of constructive scattering gives a series of points on the fluorescent screen of the TEM, this is the electron diffraction pattern. The distance "r" of the spots in the pattern is related to the . crystalline interplane spacing "d". Generally, the crystalline substance can be identified by comparing the set of "d" values with available XRD data. It can be well appreciated that the electron diffraction pattern has great potential for micro-phase analysis. However, the technique requires thin samples to transmit the electrons. Estimates of the maximum thickness of crystalline metal specimens for electron transmission at 1000 kV are 4-8 μ m for aluminum, [98] 1-2 μ m for copper [99] and 1-2 μ m for iron [100, 101]. In the case of commercial 100 kV TEM/STEM microscopy the penetration of electrons would be about an order of magnitude less. ($\approx 0.1 \ \mu m$ to 0.8 μm). Consequently, the great majority of the particles in the residues are too thick for the production of electron diffraction patterns.

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Figure I.6. General principle of the generation of an electron diffraction pattern. An electron beam with wavelength λ is diffracted by a crystalline plane with interplanar distance "d". The resulting diffracted spot is H. λ is a microscope constant obtained using known substances; 'r' is the distance between the diffracted spot and the center spot (given by the undiffracted electron beam)

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I.3 REVIEW: CHARACTERIZATION OF RESIDUES

I.3.1 Characterization of electric arc furnace (EAF) dusts from steelmaking

Goldstein et al [81] have reported extensive work on the characterization of steelmaking EAF dusts. The work was a project sponsored by the U.S Department of Commerce and included the work of 15 scientists from 4 departments of Lehigh University (Materials, Chemistry, Geology, Physics) and 3 Research Centres of the U.S. Bureau of Mines (Avondale Md., Twin Cities, Minn., and Rolla Mo.). This work, a report of approximately 300 pages, is the most extensive on the characterization of steelmaking dusts.

Goldstein et al studied 33 samples from 25 EAF steelmaking plants. The characterization was done by the following procedures:

- 1.- Weight loss during drying, density and surface area determinations
- 2.- Chemical analysis and toxicity test (EP Test)
- **3.- Size fractionation**
- 4.- Chemical Analysis as function of size
- **5.- Magnetic Separation**
- 6.- X-ray diffraction
- 7.- Characterization of particles by SEM, TEM, and EDS
- 8.- Mössbauer spectroscopy

I.3.1.1 Weight loss, density and surface area determination

Weight loss was measured at 100 °C for \approx 16hrs. Density was determined by standard pycnometry using ethanol. Ethanol was used because its wetting characteristics are superior to those of water. Negative pressure was used to cause boiling of the alcohol to eliminate entrapped air. The determined values of the density were observed to be low. The EM study indicated that this was due to the hollow sphere nature of many particles. Also, it was suspected that ethanol was partly dissolving some constituents of the sample.

Surface area was determined by the flowing gas B.E.T. method. The values found were variable from sample to sample, being from ≈ 0.1 to 8.0 m²/g.; the modal value was $\approx 3 \text{ m}^2/\text{g}$.

I.3.1.2 Chemical analysis and EP test

Initial semiquantitative chemical analysis was performed by emission spectrography. Using this technique the elemental content was divided into 15 groups: +10% (over 10%); -10+5% ... to less than 0.00001% and not detected. The elements analyzed were Ag, Al, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Ge, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Rb, Sb, Si, Sn, Sr, Ti, V, W, and Zn. The results were not quantitative, and they were used only as guideline values.

Quantitative chemical analysis of major elements was done by conventional analytical methods. Brief descriptions for some of the methods were given. All analytical methods used were tested with iron and steel standards. Minor and trace elements were analyzed by atomic absorption (AA) techniques. General descriptions of sample preparation for AA were given. Zinc as ZnO was determined by leaching with Muspratt solution (5 g NH₄Cl, 20 ml NH₄OH conc. 0.90 S.G., 50 ml H₂O) at room temperature for one-hour [165]. For the particular case of the ZnO determination, the reliability of the Muspratt method for these samples was challenged later based on findings from Mössbauer analysis and from leachability studies [187].

I > INTRODUCTION

The chemical composition of the dust samples was found to be directly influenced by the chemistry of the furnace. In general dusts from stainless steelmaking (SS) were higher in chromium and lower in zinc and lead than those dusts generated in carbon-steelmaking (CS). Correlation between the chemical composition of the dusts and the furnace size and/or dust collecting system was not found, either because it does not exist or because it was obscured by the major influence of charge type.

The Extraction Procedure, EP toxicity test [166] was performed on the dust samples. The results showed that most of the samples failed the test mainly because of cadmium and/or lead; some samples failed the test for chromium, as well.

I.3.1.3 Size fractionation

Size fractionation of the samples was performed for the following studies:

- 1.- For the determination of the chemistry of the dust as a function of size.
- 2.- To provide size fractions for characterization by XRD and EM-EDS techniques.
- 3.- As part of the studies performed to test the applicability of physical separation methods.

Dry size fractionation was ruled out because of the particle size range involved. Therefore wet size fractionation had to be used. However, for each of the studies size fractionation was performed differently. In studies 1, and 2, there was more concern about phase solubility in water, and thus size fractionation in water was avoided. In study 3, water solubility was ignored because industrial physical separation methods that use liquid media other than water are too costly and/or hazardous. Therefore in study 3, size fractionation was done in a Warman Cyclosizer (167).

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However, it must be recognized that the size fraction analysis obtained in study 3 is not accurately related to the size distribution in the original samples.

The major problem during size fractionation in studies 1, and 2 was to avoid agglomeration of the physical particulate constituents of the dusts. The agglomeration problem was solved by trying several liquid dispersion media.

In study 1, propanol was found best to avoid agglomeration. The size fractionation itself was performed by centrifuge. The size fractions were then submitted to chemical analysis.

In study 2, size fractionation was also done with a centrifuge. In this study methanol was found best to avoid agglomeration and was used for the size fractionations. However, it was suspected that methanol could dissolve some constituents of the sample. The obtained size fractions were used in the characterization by XRD and EM-EDS techniques.

I.3.1.4 Chemical analysis as a function of size

The results of the chemical analysis as a function of size showed zinc, and lead to be more concentrated in the smaller size fractions; chromium showed the opposite tendency. Of these tendencies, only the one for zinc was confirmed by XRD and SEM

I.3.1.5 Magnetic Separation

Magnetic separation was performed in two different studies:

1.- In characterization, to provide magnetic and non-magnetic products to characterize by XRD, EM-EDS and Mössbauer spectrometry.

2.- As part of the studies performed to test the applicability of physical separation methods.

I **I** INTRODUCTION

The magnetic fractionation performed in study 1, were simply done by extracting the magnetics with the help of a small permanent (weak) magnet from a suspension of dust in propanol. These magnetic fractions were characterized by XRD, EM-EDS and Mössbauer.

The magnetic separation in study 2, was performed in water and with a Davis tube (i.e. low magnetic field intensity) and with an Eriez high- intensity magnetic separator at two settings: 0.05T (500 Oe) and 0.1T (1000 Oe). The magnetic products of these techniques were not characterized by XRD, EM-EDS or Mössbauer spectrometry.

The characterization of the magnetic fractions of study 1 and the chemical analysis of the magnetic fractions of study 2, showed that the low intensity magnetic separations had some potential application for the case of the CS dusts. In general, the percentage of zinc enrichment that can be obtained by low-magnetic separation is approximately equal to the percentage of ferromagnetics in the dust. The ferromagnetics are defined as the magnetics pulled by the Davis tube. For CS dusts, the ferromagnetic content range ⁴ from 10 to 30% and zinc contents from 10 to 20%. Therefore magnetic separation could increase the zinc content from 11-13% to 22-26%.

I.3.1.6 X-ray Diffractometry (XRD)

XRD was performed on bulk dust samples, on size fractions and on magnetic separation products. In as much as only a few diffraction maxima of a minor crystalline phase in a polyphase sample may be recorded, the final results for the identified phases were drawn from integration of the XRD patterns of the different size fractions and magnetic products of a given dust sample. The XRD analyses were done using CuK_{α} radiation in conjunction with a Philips APD-3600 automated powder diffractometer.

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The results showed that the dominant phase was a spinel phase containing mainly iron and sinc; the presence of chromium and manganese in the spinel was also suspected. Another major phase often present was ZnO. Also variable amounts of α -Fe₂O₃ were found. Samples with high calcium contained calcite (CaCO₃) and/or lime. Several minor phases were found in several samples, such as: CaF₂, fcc iron, SiC, CaO, NaCl, KCl, FeO and MgO.

With the exception of ZnO, none of the crystalline phases showed any significant size dependence. The amount of ZnO relative to spinel increased with decreasing particle size.

The unit cell dimension of the spinel phases were calculated from interplanar spacing in back-reflection. From the values of the parameter a_0 , it was shown that compositional variation existed. Also it was found that the parameter a_0 of the spinel in the magnetic products was close to that of magnetite (Fe₃O₄) whereas the non-magnetic products had spinels with a unit cell approaching that of zinc-manganese ferrite.

The authors of the Mössbauer study placed more weight on the cell parameter determination by XRD. This contrasts with the more cautioned position of the authors of the XRD study. The caution is understandable since some uncertainties cannot be overlooked. For example, the XRD authors recognize that the value of the a_0 parameter was accurate to only ± 0.03 Å. On the other hand the a_0 value for spinels of the family $Zn_sFe_{3-s}O_4$ varies between 8.400 Å for Fe_3O_4 to 8.440Å for $ZnFe_2O_4$. This indicates a variation in a_0 of 0.040Å; a very close value to the accepted accuracy of ± 0.03 .

I.3.1.7 Characterization of particles by SEM, TEM, and EDS

EM-EDS studies were performed on the bulk dust samples, on the size fractions and on the magnetic separation products. One of the major difficulties encountered during sample preparation was to ensure adequate de-agglomeration of the dust for microscopy.

The specimens were prepared for SEM by dispersion of the dusts in propanol. The suspension was filtered on 0.2 μ m pore-size Nucleopore filter. The filter was cut and mounted on an aluminum SEM stub using carbon conducting cement as an adhesive. Carbon was then evaporated onto the specimens prior to SEM examination. The same dust-loaded filter was used to prepare specimens for TEM using the Jaffe Wick technique.

According to XRD, most of the phases were oxides. However, in general, an EDS system is not able to detect oxygen. The study of one sample with a windowless detector in a SEM, provided oxygen maps that substantiated that the particles were primarily oxides. Also a TEM equipped with an electron energy loss spectrometer (EELS) system was used to confirm the presence of oxygen inferred indirectly from electron diffraction patterns. Limited application of this technique was found due to difficulties arising from the typical particle thickness. However, some particles of suitable size were studied by electron diffraction-EELS and this also supported the XRD finding that most of the phases were oxides.

Once the oxide nature of the particles was proven, then particle characterization by EDS was performed. Two techniques of SEM-EDS were applied:

- 1.- Particle observation and EDS analysis by standard SEM microscopy, using secondary electron images.
- 2.- Particle observation and EDS analysis by SEM and automated image analysis (AIA).

The latter procedure allowed the analysis of many particles in a short time but it had the restriction that agglomerates were considered as single particles.

The results obtained with SEM-study 1 showed:

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- a) In general the particles were agglomerated due to sintering. The particle size ranged from 0.1 μ m to 10 μ m, the majority of which were less than 1 μ m in size. Most of the particles were found to be spherical and some were broken and hollow. From this, it was suspected that an undetermined amount of the spheres might be hollow.
- b) The major dominant phase found in all the samples was the spinel.

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- c) The products of size fractionation were found to contain particles that were, in general, larger than the size limits given in the fractionation. These particles were often porous. It was concluded that "true" size fractionation by centrifugation had not taken place.
- d) Some distinctly faceted and spherical particles of zinc oxide could be found. The latter were indistinguishable visually from the spinel spherical particles.
- e) A few particles were observed giving EDS-spectra corresponding to relatively pure oxides, viz. Fe₂O₃, CaO, SiO₂, CdO and SnO. It was suspected that in many cases the cadmium in the particles was below the detectability limit of EDS.
- f) A large number of elements were found in most dust particles.

The results of the SEM-EDS-AIA study 2 showed:

- a) In general the chemistry of the predominant particles changed from sample to sample. Some samples had predominantly Fe-rich particles, others predominantly Fe+Zn-rich particles and others predominantly Fe+Cr-rich particles, etc. This was found to be related to the chemistry of the process. To illustrate this very generally consider the following:
 - For a composite of 6 samples of CS dust, the most abundant particles were: Fe+Zn ($\approx 55\%$ of the particle population), followed by Fe- rich particles ($\approx 16\%$).

- For a composite of 2 samples of SS dust, the most abundant particles were:
 Fe+Cr (47%), followed by Fe-rich particles (≈20%).
- b) The majority of the particles in the CS dusts were either Fe-rich or Fe+Zn-rich. Particles of the group Fe+Zn showed variation in the ratio $I_{Zn}/(I_{Zn}+I_{Fe})$, where I_i is the EDS peak intensity for a given element. This, assuming the particles are to be of spinel type, means a compositional variation of the type $Zn_sFe_{3-s}O_4$.
- c) In many instances, for the CS dusts, magnetic separation succeeded in concentrating much of the iron into the magnetic portion and much of the zinc into the non-magnetic. This was generally not true for the SS dust samples.
- d) Studies were also done with dust samples collected on partially evacuated thimbles situated in the cold part of the flue of the electric furnaces. From these CS samples it was found that during the refining stage there is an increase of Fe-rich particles relative to the Fe+Zn-rich particles. Also the number of particles containing lead increased dramatically. It was suspected that probably lead or lead oxide was deposited on a core of iron particles. It was also found that if the CS dust is recycled to the furnace (a practice called greenballing addition), then the production of zinc-rich particles increased; however, the increment of the Fe+Zn-rich particles was not comparable. This was thought as evidence of not enough iron dust being produced to accommodate the zinc as zinc ferrite.

In general, XRD failed to positively identify any lead phase in the CS dusts; this was possibly due to the small amount of lead phase present. However, the authors of the SEM-EDS-AIA study, when particles with lead were found, considered it to be present as lead oxide. In spite of this it is well known (168) that lead has an extremely strong tendency to react with sulphur. This tendency is such that even a SO₂ concentration as low as 10^{-4} atm is sufficient to sulphatize PbO to

PbSO₄PbO. Therefore, it could be expected that at least part of the lead should be present as an oxysulphate. The results of the leaching tests seems to support the latter.

I.3.1.8 Mössbauer spectroscopy

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Some selected samples of CS dusts were studied by Mössbauer spectroscopy. Some products of the magnetic separations performed with the small magnet method were also studied.

It was found that the line widths and relative intensities of the magnetic lines in the Mössbauer spectra for all the specimens (except one) were similar to spectra for non-stoichiometric zinc ferrite $Zn_{s}Fe_{3-s}O_{4}$ in which 0.2 < x < 0.6. However, the Mössbauer technique was not suitable to clarify if other metal besides Zn, such as Ni, Mn, Mg and even Cr, could be present in the spinel.

Using the Mössbauer spectra, the amount of zinc ferrite was calculated. From the calculated amount of zinc ferrite, and the total amount of zinc, then the amount of ZnO was calculated. The Mössbauer-ZnO was higher than the Muspratt-ZnO by an average of 22 %.

Mössbauer spectrometry showed that some CS dust samples had upgraded levels of $Zn_zFe_{3-z}O_4$ (0.6<x<1) in the non-magnetic fraction.

I.3.1.9 Physical and Chemical separations

The report by Goldstein et al [81] also presents results of physical and chemical separations. This thesis will review only those results that are closely related to the characterization of the dusts.

The results of the physical and chemical separations indicated that the CS and the SS dusts were inherently different. No chemical separation method succeeded in giving promising results for the SS dusts. This was due to the fact that their high chromium and low sinc contents made them more refractory and therefore restricted chemical dissolution. The physical methods tried (tabling, flotation, flocculation, and magnetic separation) for the SS also failed to give an appreciable enrichment of any of the elements of interest (Fe, Pb, Zn, Cr, Cd). On the other hand, for CS dusts, magnetic separation showed some potential for sinc enrichment in the non-magnetic and iron enrichment to the magnetic; however, there was no clear cut separation.

From the standpoint of characterisation, two of the leaching tests with the CS dust are interesting, the leaching with Muspratt solution and a leaching using a potentiometric titration with H_2SO_4 to an end pH of 3.5. The Muspratt [165] test is deemed to dissolve free ZnO present in the samples. On the other hand the H_2SO_4 -potentiometric titration corresponds to low acid leaching conditions, and therefore is also deemed to dissolve easily soluble zinc. The results of the Muspratt leaching showed that 59% Zn was dissolved at 75 °C (only 54% at 20 °C). On the other hand, the pH 3.5 sulfuric titration dissolved 69% Zn. From these results the authors concluded that the Muspratt method was not effective in determining free ZnO, and that the pH 3.5 sulfuric titration is better to determine readily soluble ZnO. This conclusion was supported from the ZnO inferred by Mössbauer spectrometry. Therefore the composite sample of the CS dust appears to have approximately 69%Zn as ZnO.

The results of the leaching with NH_4Cl and NaOH are also interesting from the point of view of characterization. The leachings with 25% NH_4Cl and with 25%NaOH extracted 44% and 63% of the lead respectively. The residue of the NaOH leach analyzed only 0.05%S, indicating that lead in that residue was not further present as sulphate. From these results it was inferred that lead was present in the original CS dusts in at least two different phases. But no possitive identification was given.

I.3.1.10 Conclusion of EAF characterization

The work by Goldstein et al contains results of other studies involved with the recovery and recycling of EAF. For example it describes possible pyrometallurgical processes for the decomposition of sinc ferrite into ZnO and iron oxides and also gives an assessment of the present methods for the recovery and recycling of EAF dusts. Since these studies are not strictly related with the characterisation of residues they are not reviewed in this thesis.

In general the conclusion of Goldstein et al is that sinc ferrites are a major zinc phase in the CS dusts; sinc recovery from ferrites by pyro or hydrometallurgical methods is difficult. Zinc oxide, the other major sinc phase is easily leached. There are processes to recover sinc from sinc ferrites, but these processes are more costly than those for ZnO. Also, these processes have a lower limit of sinc content in the materials that can be processed economically. For example, the Waelz kiln process [85] could treat the EAF dusts and is economic if the zinc content in the dust is approximately 20%. (another source [169] quotes 15% Zn at a capacity of 50,000 tons/year of dust). On the other hand chemical separation process are more attractive because capital requirements for a small plant are far less than those of pyrometallurgical processes. However the economic limit zinc content is said to be \approx 40 %Zn. Because many CS dusts do not reach this limit, alternatives for zinc enrichment are proposed. One enrichment method may be magnetic separation. Unfortunately some CS dust are not enriched sufficiently by magnetic methods. Another alternative is based on the suspicion that recycling of the EAF dusts through greenballing would enrich not only the zinc content but also the amount of ZnO relative to zinc ferrites. It should be noted that magnetic concentration might be still applied to these enriched dusts. Nevertheless the full impact on the EAF operation due to greenballing of CS dusts is not fully substantiated in the Goldstein et al. report. Another important factor for the economical treatment of

EAF dusts is the proximity of the retreatment plant to the dust sources.

The SS dusts have a low content of sinc, and sinc oxide or sinc ferrite are no longer the dominant phases. On the other hand they contain higher values of alloy elements as chromium and manganese. This makes them more refractory to treatment by any physical separation method, and increases the difficulties of their treatment by hydrometallurgical methods. However the inherent value of the alloying elements in the SS dusts have made the recycling of SS dusts to the EAF commercially practical.

I.3.2 REVIEW: Characterization of Cu-Smelter Cottrell dust

Scott, 1984 [145] and Dutrizac and Chen, 1983 [94] have performed some characterization work on Cottrell dust from the copper smelter of Kidd Creek. The characterization performed by Scott [145] was of a practical nature and based mainly on standard wet chemical analysis, XRD and optical microscopy of polished specimens. Scott found that the major phases present were zinc ferrite $ZnFe_2O_4$, and metallic copper. It was considered that all the zinc was present as zinc ferrite and the residual iron was present as magnetite. From this assumption it was calculated that magnetite was a major phase present. Estimations from optical microscopy showed that Cu_2O was present in quantities of $\approx 5\%$. It was also found that the ferrite was optically homogeneous.

The characterization performed by Dutrizac and Chen [94] was experimentally more rigorous; therefore this work will be reviewed in more detail. Dutrizac and Chen [94] characterized two Cottrell dust samples from the Kidd Creek copper smelter. This work was generated because Kidd Creek encountered problems with the recycling of the Cottrell dust in their zinc leaching plant. The problems were associated with high levels of Fe^{+2} in the solutions, presumably leading to a premature precipitation of jarosite in the circuit. Therefore, the characterization of the dust samples was planned to help explain those problems.

The following techniques were used to characterize and study the Cottrell dust samples:

1.- Wet chemical analysis

2.- Mössbauer spectrometry

3.- Leaching with water and with H_2SO_4 solutions (6 g/l Fe⁺³ and 50 g/l H_2SO_4)

4.- XRD (Debye-Scherrer camera)

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5.- Optical microscopy (OM) and SEM-EDS

I.3.2.1 Wet Chemical Analysis and Mössbauer spectrometry

Non specified chemical wet analyses were performed to determine the following elements: Cu, Fe, Zn, Pb, Na, K, As, Sb, Ag, S_{TOTAL}, and S^o + S⁻². Efforts were made to determine Fe⁺² and Fe⁺³ using wet chemical methods. These were abandoned because numerous side reactions affected the reproducubility of the results. Finally Mössbauer analysis was the preferred method for the determination of ferric and ferrous iron. The samples analyzed had approximately 15 %Cu, 6 %Fe and 20 %Zn. Sodium and potassium, two elements of interest from the point of view of jarosite precipitation were found at too low concentrations (≈ 0.05 % and ≈ 0.13 % respectively) to cause premature jarosite precipitation.

Only qualitative Mössbauer spectrometry was performed, but this was sufficient to support the premise that virtually all the iron was present in the Fe^{+3} form. This was logical due to the oxidizing nature of the smelting procedures employed at Kidd Creek.

I.3.2.2 Leaching Tests

All the leachings were done in air for 1 h. at 30°C using 25g of dust in 250 ml of solution. It was found that negligible iron dissolution resulted from water leaching; however, there was a copper extraction of $\approx 20\%$. The measured extent of alkali dissolution in water was 100%.

Acidic ferric sulphate leaching was found to dissolve a modest amount of iron $(\approx 25 \%)$; and approximately 77 % of the copper.

Experiments under laboratory conditions failed to simulate the premature precipitation.

I.3.2.3 X-ray Analysis

XRD analysis of the Cottrell dusts revealed the presence of the following major phases: $PbSO_4$, $CuSO_45H_2O$, $ZnOFe_2O_3$, $ZnSO_4H_2O$, $(Cu,Fe)SO_4H_2O$ and SiO_2 . Trace amounts of Cu_2O and CuO were also found. The XRD spectra showed evidence for the presence of many other minor phases, but they could not be conclusively identified.

XRD of the residues of the leach tests revealed that the major phases not dissolved were $PbSO_4$ and $ZnOFe_2O_3$. It was found that leaching effectively removed zinc sulphates, copper sulphates and copper oxides. The residue of the acidic leach also revealed the presence of $Cu_{1.8}S$. This product was suspected to be related to the alteration of copper sulfides due to the acid leach.

I.3.2.4 Optical Microscopy (OM) and SEM-EDS

The residues were mounted in polished sections and studied by OM and by SEM-EDS. However no results of optical microscopy were presented. On the other hand, all the presented microscopic information is related to SEM using SEI and BEI images; EDS analysis was also performed.

SEM showed that the dusts consisted of coarse spheres, presumably solidified drops of oxides, sulphides etc. surrounded by much finer dust or fume particles. The finer particles were often $\leq 1 \ \mu m$ and could not be analyzed accurately. From the SEM-EDS study of the large spheres the following results were obtained:

- a) A large proportion of the spheres consisted of copper oxide or Cu-Fe-Ca oxides, often co-existing as complex intergrowths. Occasionally, the second phase also contained traces of Zn, Pb and S.
- b) Metallic copper spheres were found, often rimmed or intergrown with Cuoxides or with Fe-Cu-Zn oxides.

- c) Spheres of copper oxides were also observed. The authors state that spheres of Cu₂O rimmed with CuO could be observed.
- d) Spheres of copper sulphides often with rims of copper sulphates were found.
- e) The observations of the leach residues confirmed that copper, copper oxides and copper sulphates had been largely dissolved. However copper sulphides were still plentiful. The authors mentioned that the copper sulphides appeared to be altered to covellite. Numerous grains of zinc ferrites were also found in the leach residues, sometimes containing traces of Sn, Cu, or Pb.

I.3.2.5 Conclusion of Review of characterization of Cu-smelter Cottrell dust

Comparison between the characterization of the copper smelter Cottrell dusts by Scott [145] and by Dutrizac and Chen [94] shows some obvious differences. The characterization performed by Dutrizac and Chen [94] is more extensive. Scott inferred the presence of magnetite and does not report the presence of PbSO₄. In contrast, Dutrizac and Chen did not report the presence of magnetite as a major phase. The two characterizations agree, however, that the presence of metallic copper is important.

The statement made by Scott that the zinc ferrite is homogeneous is based on optical microscopy. Dutrizac and Chen do not elaborate on this particular point; however, it can be seen from their SEM observations that typically the particles (agglomerates) in the dust are composed of several phases.

The work reported by Dutrizac and Chen shows clearly the practical application of the characterization of residues to improved understanding of the possibilities of recycling and retreatment. From the gathered information of the characterization it is shown conclusively that the high amounts of Fe^{+2} found in the industrial leaching solutions do not come from the Cottrell dust itself. The high amounts

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of Fe^{+2} in the industrial leach process was explained by the substantial amounts of copper phases present in the dust (as metallic copper, as oxides, as sulphides and as sulphates). The copper phases promote the reduction of Fe^{+3} to Fe^{+3} . The source of Fe^{+3} could be the Cottrell dust itself or the ferric sulphate present in the leaching solutions. Therefore, if Cottrell dust is fed to the zinc leach circuit, a strong oxidation step in the leaching solution must be provided or, as Donyina [92] points out, the Cottrell dust can be treated separately. Based on the presence of metallic copper particles, Dutrizac and Chen proposed a more careful segregation of the dust from the first banks of the Cottrell precipitator to recycle most of the metallic copper particles to the copper smelter. It also is obvious that a pre-water leach will reduce the copper water-soluble components in the recycling feed to the zinc plant. The reasons for premature jarosite precipitation were not elucidated.

From the results of the SEM studies, it is possible to see that the authors were capable of discriminating between:

- Cu and Cu-oxides.

- Cu₂O and CuO.
- Copper sulphides and "covellite" (although not clearly specified in the paper this could mean discrimination between chalcocite, Cu₂S and covellite, CuS; or even between Cu₂S and digenite Cu_{1.8}S).
- Copper sulphides and copper sulphates.

The method of discrimination between the phases is not clearly elucidated by the authors. However, as several backscattered-electron (BE) images are presented, it can be inferred that the method of discrimination was performed using EDS spectra and the BE image. However, using solely EDS and BE information it is difficult to differentiate between some of the mentioned phases. Hence it is possible that the authors used information gathered by or by other techniques [96] to be able to

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perform the mentioned discrimination in the SEM. This is an important consideration: in the characterization of complex materials it is necessary to integrate the information gathered by different analytical techniques.

The sample preparation method used for SEM by Dutrizac and Chen contrasts with that used in the characterization of EAF dust by Goldstein et al. [81]. The methods, polished specimen and substrate specimen, represent the two most commonly used methods of sample preparation for electron microscopy of particulate materials. Each has its advantages and drawbacks. Polished specimens are obtained using resins to disperse the particles, once the resin is hard, the samples are then polished. The polished specimen preparation method produces a flat surface that is easier to analyze due to the absence of geometrical effects between the sample and the X-Ray detector [139]; it also allows easy identification and observation of cored-type particles. However particle dispersion in the mounting resins is difficult. Dilution, of the sample with solid particles known not to be present in the samples may be used [184] to improve the separation between the particles. However, even using such methods, the separation of the fine particles typically encountered in the dusts is hampered. Because of this, sometimes, only the coarser grains present in the polished sections are analyzed quantitatively by EMPA. Also it is known that mechanical polishing of the samples may alter chemically the samples and special precautions must be taken to avoid that (an example of this is given by Remond et al [170]). Physical sample alteration also occurs when the sample contains phases with very different hardness, this may produce steps in the phase boundaries or even lifting of the softer phase. On the other hand the substrate specimen has the advantage of less alteration of the sample and shows better the surface morphology of the samples. However, the geometrical effects between the sample and the X-ray detector may be serious and give less accurate chemical analyses. To alleviate this high take off angles (i.e. increasing the vertical distance between the detector and the sample) have been recommended [139].

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I.3.3 REVIEW: Characterisation of Residues from Zinc Hydrometallurgical Treatment

About 85% of the world's sinc currently is produced by the roast-leach-electrolysis process whereby sinc sulphide concentrates are roasted in air to form SO₂ gas and a calcine consisting mostly of ZnO and ZnOFe₂O₃ (sinc ferrite). Zinc oxide is readily soluble in H₂SO₄. But sinc ferrite is more refractory and leaching with hot and concentrated H₂SO₄ (>90 °C and H₂SO₄ > 35 g/l) must be used for dissolution. Therefore, the general practice is to include at least two steps of H₂SO₄ leaching. Iron which also dissolves during acid leaching, can be rejected from the circuit as a readily filterable precipitate by the jarosite, goethite or hematite processes [174, 175]. Alternatively, the pressure leach process developed by Sherritt Gordon Mines [176-178] can be used. In this process the zinc sulphide concentrate is leached at temperatures of ≈150 °C and under an oxygen partial pressure of 207 kPa. This process has the advantages of forming elemental sulphur and that pyrite in the feed is not significantly attacked. Consequently, pyrite rich concentrates can be processed by this method without the need for extensive iron control circuits.

Several papers on the characterization of the residues from hydrometallurgical zinc processes have been published [95, 96, 120, 148, 185]. A brief review follows on the characterization of these residues.

I.3.3.1 Review: Mineralogical characterization of residues from the Kidd Creek zinc plant

Owens, 1981 [148] performed characterization of residues from the hydrometallurgical zinc plant of Kidd Creek. Three residues were studied: the neutral leach residue, the high acid leach residue and the jarosite residue. However, these residues resulted not from the normal operation of the plant but from a test-run on roaster precipitator dust of the same Kidd Creek complex.

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The methods used for the characterization included XRD (Debye-Scherrer camera) and microscopy. The latter was performed using polished samples and optical methods as well SEM-EDS, and EMPA.

The neutral leach and the high acid leach residue were more difficult to study since the majority of the particles were less than 20 μ m and many were smaller than 1 μ m. Besides these particles were agglomerated by a gel-like component of complex composition. The gel posed a problem in that it was unstable under the electron beam. On the other hand the jarosite residue was easier to study by EM methods since the gel-like binder was absent.

XRD showed that sinc ferrite was the major crystalline phase in all three residues. Sodium jarosite $(NaFe_3(SO_4)_2(OH)_6)$ was a major phase in the jarosite residue. Sodium jarosite was also found in minor abundance in the leach residues. Quartz was a trace phase in the leach residues. XRD showed that the major difference between the leach residues was that the high-acid leach residue contained gypsum in minor quantities.

Besides the major phases identified by XRD several minor phases were identified by electron microscopy. It was found that the occurrence of silver-bearing phases could only be identified in the high-acid leach residue. The gel-like binder in the leach residues was analyzed by SEM-EDS. Despite its instability under the electron beam, the gel in the high-acid leach residue appeared to be, on average, richer in its silica content than the one found in the neutral leach.

PbSO₄ was expected to be present in the neutral leach residue. However, lead was found mainly as a minor to trace element in various phases in all three residues. It was concluded that because of its morphological and compositional complexity its presence in the leach residues could not be defined. The EMPA analysis of the natrojarosite in the precipitation residue showed that the lead occurred either as a variable and minor element substituting for sodium in this phase, or as minute, imperceptible inclusions of lead jarosite.

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Finally, no silver phases were found in the jarosite residue, and if silver was present it was below the detection limits of the EMPA (≈ 250 ppm of silver in natrojarosite).

It is interesting to notice that Owens [148] could discriminate between sulphide and sulphates based on a shift in the wavelength of the S K_a emission line, which is a result of differences in chemical bonding.

I.3.3.2 Review: Characterization of Jarosite residue from the pressure leach at Cominco Ltd.

The residues formed during autoclave leaching of zinc concentrates at Cominco Ltd, Trail, B.C. have been characterized by Dutrizac and Chen, 1983 [95].

The slurry from the autoclave is flashed to atmospheric pressure and floated to remove the elemental sulphur formed in the autoclave. The flotation tailings are the jarosite residue that was characterized by Dutrizac and Chen. Several samples from different autoclave compartments were also taken to characterize the residues at the different stages of the autoclave process.

In addition to classical chemical analysis, the following experimental techniques were used: cyclosizing, Debye-Scherrer and Guinier-deWolff XRD, SEM-EDS and EMPA. The Guinier-deWolff XRD analysis was used because it has the benefit of detecting trace amounts more easily.

All the samples for electron microscopy studies were mounted in polished sections. Before mounting the samples, the elemental sulphur present was removed. The presence of elemental sulphur in the samples can create problems during mineralogical investigation. For example, in loose powder mounts, the sulphur tends to coat and agglomerate other species; in polished sections, the sulphur lifts out possibly taking other constituents with it as well. Therefore elemental sulphur was eliminated by CS₂ extraction in a Soxhlet reactor. EMPA analysis was performed on some of the coarser grained material obtained by Cyclosizer.

The collected results showed that the residues consisted predominantly of lead jarosite (<20 μ m) together with lesser amounts of elemental sulphur, lead sulphate, silicate minerals and traces of residual sulphides (chalcopyrite, pyrite, sphalerite and pyrrhotite).

The lead jarosite contained minor amounts of potassium substituting for lead and zinc replacing trivalent iron as well as traces of silver which also substitutes for lead. The results suggested that galena is rapidly oxidized to PbSO₄ which then reacts with ferric sulphate to form lead jarosite incorporating potassium, zinc and silver. Apparently the formula of the jarosite produced is $(Pb,K,Ag)_{z}(Fe,Zn)3(SO_{4})_{2}(OH)_{6}$. There was no positive identification of separate hydronium jarosite or potassium jarosite phases. EMPA studies of the coarser lead jarosite grains found them to contain silver in small but variable concentrations. The average silver concentration and the relative amounts of the jarosite phase formed suggested that the lead jarosite is the dominant silver carrier; no other silver phases were detected.

The cyclosized fractions of jarosite were leached with ammonium acetate to dissolve the PbSO₄, the residues of this leaching were analyzed by XRD, and it was found that the remainder of jarosite had cell parameters consistent with published values [171].

I.3.3.3 REVIEW: Characterization of residues from pressure leach of a sulphide concentrate from New Brunswick

Dutrizac and Chen have characterized other residues, for example they have characterized the residues of a leach test performed by Sherritt Gordon using a two step pressure leaching of a Zn-Pb-Cu-Ag concentrate prepared from a New Brunswick massive sulphide ore [96].

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The experimental techniques used for the characterization were similar with respect to those used earlier [95] by the same authors (see section I.3.3.2). For the sample preparation, besides using the polished section technique, they also prepared some substrate samples. These samples provided some extra information about surface morphology that is not provided by the polished mounting technique.

The characterization that they performed was with special emphasis on silver. It was found that silver reports in the final leach residue mostly as unleached argentian tetrahedrite and precipitated silver-bearing lead jarosite. Other silver carriers identified included silver bearing PbSO₄, unleached galena and basic iron sulphate gel particles containing silver sulphides.

They found that screening and/or flotation of the leach residue yields a sulphursulphide fraction which contains most of the unleached argentian tetrahedrite.

The results showed that treatment of the remaining jarosite-rich fraction by reductive SO_2 leaching converts the silver-bearing jarosite to silver-free PbSO₄. The silver liberated during this reaction ultimately precipitates as large complex sulphide-sulphate capsule-like structures rimmed by silver sulphides.

I.3.3.4 REVIEW: Characterization of the residue from the super hot acid leaching of Vieille-Montagne

Dutrizac and Chen, 1987 [120] have also performed characterization of the super hot acid leach residue produced at Vieille-Montagne, Belgium. The hydrometallurgical zinc plant of Vieille-Montagne includes neutral, hot acid leaching and super hot acid leaching (>90 °C with >100 g/l H₂SO₄). Unwanted dissolved iron is rejected by the goethite process [172]. The final residue of the leachings is washed and is sent to a two-step flotation process. The first flotation concentrate is deemed as a silver concentrate and consists principally of elemental sulphur and

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unleached sphalerite which seems to collect the silver present. The second flotation step, performed with the tailings of the first flotation, is aimed to produce a lead concentrate which is mainly PbSO₄, this provides an additional silver recov-Although the principal objective of hot acid leaching is to dissolve any zinc ery. present as ferrite, a further role, especially of the super hot acid leach, is to decompose any jarosite-type compound [(K,Na,Pb,Ag)Fe₃(SO₄)₂(OH)₆] which may have formed in either the neutral or conventional hot acid leaching circuits. Silver- and lead-bearing jarosites are not recovered extensively during flotation and because of their relatively low silver and lead contents, they tend to reduce the grade of the flotation concentrate. Therefore jarosite-type compound must be decomposed before flotation. Various studies (173) have suggested that acid concentrations of at least 100 g/l H_2SO_4 are required to liberate the silver and to form PbSO₄ from the jarosites; such conditions are satisfied in the super hot acid leaching. A further objective of super hot acid leaching is to complete the ferric sulphate oxidation of residual sphalerite present in the original calcine.

The experimental techniques used in the characterization of the super hot acid leach residue were similar to those used previously by the same authors (see sections I.3.3.2 and I.3.3.3). In addition to these, the following selective leachings for ≈ 1 h were performed to differentiate the various forms of silver and lead present in the residues:

- Leaching with 3M NaCl solution at 50-60 °C, intended to dissolve AgCl.
- Leaching with 30% ammonium acetate solution at 50-60 °C, intended to dissolve PbSO₄.
- Leaching with a solution of 20 g/l of thiourea, 2 g/l of Fe(SO₄)1.5 and 15 g/l H_2SO_4 at 30°, intended to dissolve AgCl and Ag₂S.

It must be pointed out that the results of the selective leachings must be considered indicative only. The reason for this is that the EM studies showed the presence of a silica gel that encapsulated many grains. This probably, reduces the effectiveness of dissolutions.

From the collected experimental data it was found that the super hot acid leach residue contains $\approx 25 \% SiO_2$ as silica gel and $\approx 20 \% Pb$ as PbSO₄. The silica gel likely originates from the concentrated acid attack of the silicates present in the calcine. The gel collects smaller grains of jarosite, PbSO₄, sulphur and zinc ferrite. EMPA analyses indicated that the PbSO₄ contained <150 ppm Ag.

Despite the hot acid leaching conditions, a considerable amount of jarosite remains in the residue. Jarosites that were of the type $(K, Pb, Na, Ag)(Fe, Al, Zn, Cu)_3(SO_4)_2(OH)_6$. The amount of silver in the jarosite was less than 1%. According to the selective leachings, $\approx 90\%$ of the silver is as AgCl. However this phase was not detected even after a prolonged and careful SEM-EDS search using residues whose PbSO₄ components were removed. The selective leachings also indicated that $\approx 7\%$ of the silver is as Ag₂S. This latter phase was observed in the EM studies.

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A number of other phases were also found present in the super hot acid leach residue. Elemental sulphur is a minor constituent of the residue. The leachings with CS₂ indicated that ≈ 38 % of the total sulphur is as elemental sulphur. Despite the severity of the hot acid leachings, some sphalerite was still found present. An interesting feature of the sphalerite was its low iron content, suggesting that high-iron sphalerites are easier to leach. Many zinc ferrite grains were found still present. Finally, occasional particles of Fe₂O₃, FeS₂, SiO₂, BaSO₄, and silicates were detected.

I.3.3.5 REVIEW: Characterization of residues from sulphation roastleach of complex sulphides

Espinosa et al [185] have performed characterization of the residues from a sulphation roast-leach process performed on a Zn-Cu-Pb-Ag-Fe complex sulphideore from New Brunswick. The ore was roasted to sulphatize the sulphides and then treated with a neutral acid step followed by a hot H_2SO_4 leach. The residue contains virtually all the original iron as Fe_2O_3 , and lead as $PbSO_4$, silver and any silicates. Among other studies, they characterized the neutral acid leach (NAL) and the hot acid leach (HAL) residues. They also implemented magnetic separation of the NAL and HAL residues and examined mineralogically the magnetic products.

The residues were found to be fine, approximately $80\% -10 \mu m$, $50\% -3 \mu m$. Preparation of polished samples appeared to be difficult. Therefore, only samples of the $+10 \mu m$ fractions were examined by optical microscopy. The phases present were easily distinguished in the coarse sized fractions by optical microscopy. The phases identified in the NAL were sinc ferrite, marmatite, Fe₂O₃, PbSO₄, and SiO₂. Many of the particles were found to be of multiphase character. In contrast, only Fe₂O₃, PbSO₄, and SiO₂ were evident in the HAL residue. The degree of liberation of the PbSO₄ present in the +10 μm fraction of the HAL residue was approximately 90%. From this, they elucidated that the PbSO₄ should be well liberated in the most abundant -10 μm fraction.

The NAL and HAL residues were magnetically fractionated with a Frantz separator. Their results for the NAL residue showed that zinc reports both in the magnetic product as ferrite and in the non-magnetic product as marmatite. This suggested that magnetic recovery of zinc from the NAL residue to recycle was not feasible. The Frantz analysis on the HAL residue revealed good separability of the Fe₂O₃ from the PbSO₄. Therefore high gradient magnetic separation tests (HGMS) were performed with the HAL residue. 89 %Pb was recovered in the non-magnetics; however, the separability of Fe₂O₃ from PbSO₄ was not high.

I > INTRODUCTION

The magnetic products were studied by STEM to asses the limits of the magnetic separation. Apparently samples for STEM were prepared by filtration on Nucleopore membranes. Essentially the STEM results showed that fine Fe₂O₃ particles (-10 μ m) was present in the non-magnetic product. It was inferred that this hematite was too fine to be trapped in the HGMS tests.

I.3.3.6 Conclusion of Review on Characterization of residues from zinc hydrometallurgical plants

The experimental techniques used for the characterisation of residues from sinc plant residues are based on electron microscopy techniques backed by X-ray diffraction and some differential leachings. Optical microscopy methods have been used on coarse grained material. Samples containing sulphur were leached to facilitate the preparation and to avoid sulphur coatings on particles of interest. Some substrate sample preparation has been used to obtain morphological information not disclosed by flat polished specimens. It can be assumed that the residues containing fine particles caused problems due to agglomeration of these particles with the resins used in the preparation of polished specimens. This explains why EMPA analysis was nearly always performed on large particles in the specimens. Most of the characterizations have been performed on bulk samples of the residues. Some characterization has been done using the fractionation of the residues by size or by chemical solubility or by magnetic susceptibility.

Zinc ferrite plays an important role since it is often a major phase in the residues of the neutral and the hot acid leach and also in the jarosite residue. The jarosite residue can incorporate in its composition several elements, its general formula as given by Dutrizac [179] is $MFe(SO_4)_2(OH)_6$ where M could be Na⁺, K⁺, NH⁺₄, H₃O⁺, Ag⁺, $\frac{1}{2}Pb^{+2}$. Therefore the jarosite residue could be natrojarosite, potassium jarosite or lead jarosite, depending mainly on the chemistry involved during precipitation. Silver can be incorporated in the jarosite. To facilitate the recovery of silver, the silver bearing jarosite can be decomposed with extreme leaching conditions (e.g super hot acid leaching or SO₂ leaching). In the case of Vieille-Montagne, the main silver carrier in the super hot acid is probably AgCl. However this is probably collected by sulphur agglomerates.

Gel-like silicates have been observed in some of the residues. These gels could play a detrimental role in the process due to coating and agglomeration of other phases. These gels also make more difficult the characterization of the residues.

I.4 INTRODUCTION TO THE METHOD OF CHARAC-TERIZATION USED IN THIS THESIS

It is interesting to note that zinc ferrite plays an important role in the residues of EAF, in the Cu-Smelter dusts and in the residues from zinc-hydrometallurgical plants. To aid characterization of EAF dusts, magnetic fractions were used. This is understandable since zinc ferrite is paramagnetic. However magnetic fractionation has not been as fully exploited as possible in the characterization of Cu-smelter dusts and in the zinc-plant residues. In this thesis magnetic fractionation is used extensively. Also the potential of the application of magnetic separation to these residues is explored.

This thesis deals with three residues:

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- 1. Cu-smelter dust from Kidd Creek
- 2. Jarosite and hot acid leach residue from the zinc plant of Kidd Creek
- 3. Low-acid-leach residue from the Canadian Electrolytic Zinc plant

The Cu-smelter dust studied in this thesis is not exactly the same as the one characterized by Dutrizac and Chen [94]. In the present case most of the copper particles have been recycled to the Cu-smelter and the copper water-soluble component have been removed.

The residues from the Kidd Creek zinc plant studied in this thesis are not the same as the residues studied by Owens [148]. The latter residues were generated in a leach test with the zinc Kidd Creek plant. Also Owens [148] did not used fractionation of the bulk samples for characterization.
The residues studied in this thesis were fractionated in different ways:

- 1. Using their differences in size (i.e. by cyclosizing).
- 2. Using their differences in leachability in H_2SO_4 .
- 3. Using their differences in magnetic susceptibility.

The original bulk residues samples and the fractions were studied by AA, XRF, XRD and STEM-EDS or SEM-EDS. The fractionation of the original residues was a powerful aid in the characterization of the residues. This is because the fractions are less complex than the original residues. Therefore, many phases were positively identified only after the fractions were studied. This is specially true for XRD where, for minor phases, only a few maxima may be recorded impeding their positive identification even using automated search-match programs. Finally, EM studies of the fractions are made easier if bulk phase information from XRD is available.

Magnetic fractionation was performed with the Frantz isodynamic separator. Also magnetic separations with an Eriez high gradient magnetic separator were tried. The fractionation with the Frantz separator isolated fractions with only small differences in magnetic susceptibility. This allowed the collection of information that could be not obtained in any other way.

Samples for EM examination were prepared in substrate form. Polished sample preparation was tried initially but was abandoned, since sample dispersion was poor and plucking of softer phases caused material loss and surface pitting.

SECTION II

EXPERIMENTAL TECHNIQUES

II.1 SCOPE OF SECTION II

Some aspects of the experimental techniques used for the characterization are explained in the Manuscripts presented in this thesis. This section provides a more detailed description of the techniques.

First, this section provides details about the key experimental techniques used for the characterization of the several residues that are dealt with in this thesis. These techniques were XRF, AA, XRD, and EM (either SEM-EDS or STEM-EDS).

Second, a description is provided of the experimental methods used for specific gravity determination.

As indicated in the Introduction the fractionation of the residues provided a powerful aid to their characterization. Therefore, in this section details about the following fractionations are given: size fractionation with Cyclosizer, magnetic fractionation with Frantz separator and magnetic fractionation with a high gradient magnetic separator (HGMS). The latter technique was also used to explore the potential of magnetic separation.

This section also provides details on the thermodynamic analysis used to facilitate the identification of the XRD spectra of samples from the Cu-smelter dust.

II.2 PYCNOMETER AND NULL GAS PYCNOMETER

The specific gravity of the solids was determined both by pycnometer and null gas pycnometer.

II.2.1 Pycnometer

The formula used for the determination of the specific gravity of the solids with a pycnometer (or specific gravity bottle) is as follows: [112]

$$\delta_{\bullet} = \frac{M - P}{(W + M - P - S)\delta_l} \tag{II.1}$$

where:

- δ_s = Specific gravity of sample P = Weight of empty pycnometer M = Weight of pycnometer with solids S = Weight of pycnometer with solids and full with liquid
- W = Weight of pycnometer full with liquid
- δ_l = Specific gravity of liquid

The liquid used for the measurements was water or 2-propanol. The latter was used when the sample had components which were soluble in water.

II.2.2 Null Gas Pycnometer

Specific gravity of solids was also determined by using a null-gas pycnometer (Quantachrome Corporation). This unit has the advantage that possible disso-

lution of the sample in liquids is avoided. The null-gas pycnometer is less well known than the standard pycnometer, and therefore, requires some description and explanation of its working principle:

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Figure II.1 is a schematic of the null-gas pycnometer. The sample holder is a cylindrical container of 4 cm ϕ by 10 cm length (upper left corner). However the actual sample-cell-holder volume includes all the area shaded in Figure II.1.

A sample of known weight (P) is placed inside the sample holder. The task of the instrument is to determine the sample volume. (Knowing the volume, the calculation of the sample specific gravity is a simple matter). The sample volume is determined by hermetically sealing the cell. When the syringe "S" is depressed, the pressure in the cell holder increases and the differential gauge "G₁" indicates a pressure difference. Gas is allowed to flow under pressure through needle valve "N₁" and valves "D₁" and "T₂" to pressurize "G₂" and rebalance or null the gauge "G₁". When gauge "G₁" is exactly nulled, the reading of gauge "G₂" is taken. If



Figure II.1. Schematic view of the gas-null pycnometer

this procedure is repeated without sample in the cell, then from the two readings

taken on " G_2 " the sample volume can be calculated by [113]:

$$V_{e} = V_{c} \left\{ 1 - \frac{P_{2} - P_{1}}{P_{2'} - P_{1}} \right\}$$
(II.2)

where:

- V_{\bullet} = Sample volume [cm³]
- V_e = Volume of sample cell holder. Determined by calibration with a metal cylinder of known weight and known specific gravity
- P_2 = Reading of "G₂" when "G₁" is nulled with no sample in the cell
- $P_{2'}$ = Reading of "G₂" when "G₁" is nulled with sample in the cell
- P_1 = Reading of "G₂" when cell holder is opened to atmosphere

If the G_2 gauge is properly zeroed prior to each measurement, then the equation to calculate V_s is simplified to:

$$V_s = V_c \left(1 - \frac{P_2}{P_{2'}} \right) \tag{II.3}$$

and finally:

$$\delta_s = \frac{P_s}{V_s} \tag{II.4}$$

II > EXPERIMENTAL TECHNIQUES

II.3 CYCLOSIZER

Particle size analysis was performed with a Warman Cyclosizer. The Cyclosizer is a series of five hydrocyclones with progressively decreasing inlet and vortex finder outlet diameters and fitted with apex-chambers to retain particles (Figure II.2). The design gives multiple sorting in each hydrocylone and separation becomes quite sharp compared with a conventional hydrocyclone.

The Cyclosizer is in principle an elutriator, because it separates a sample into specific size fractions by a technique which depends on the forces produced by the relative velocities of the particle and the elutriating fluid. Particles which have hydrodynamic similarity (same free-falling velocity) will be collected within the apex chamber of a given cone. The results of the Cyclosizer are reported as an equivalent particle size which is the diameter of spherical particles with the same settling rate as those particles collected in a cone.

The unit is precalibrated with a standard material with a nominal cut-off size for each cyclone (d_{∞}) based on infinite elutriation time and a set of standard operating conditions. The calibration d_{∞} values for each cyclone are:

Table II.1. Standard equivalent particle size for the Cyclosizer cones

Cyclone No	Equivalent Particle size
1	$44 \ \mu m \pm 2$
2	$33 \ \mu m \pm 1$
3	$23 \ \mu m \pm 1$
4	$15 \mu\mathrm{m} \pm 1$
5	$11 \ \mu m \pm 1$

The operating variables for the calibration are water flow rate, 11.6 l/min; water temperature 20 °C; and particle density 2.65 g/cm³.

The particle size is corrected by using correction factors that consider the test operating condition:

$$de = d_{\infty} f_1 f_2 f_3 f_4$$
(II.5)

where:

$$de =$$
 Effective equivalent particle size
of a cone
 $d_{\infty} =$ Calibration of equivalent particle size
 $f_1 f_2 f_3 f_4 =$ Correction factors for temperature,
particle density, flow rate and

time, respectively. [114]

To determine the size distribution of the samples, a known weight was wetscreened on a 200-mesh screen, the oversize was dried and weighed; the undersize was left overnight and decanted to yield a slurry of $\approx 200 \text{ cm}^3$; a small amount of wetting agent was then added ($\approx 0.1 \%$ vol of Aerosol OT, Fisher Sc. Co.). The resulting slurry was agitated with a mechanical stirrer and, at the same time agitated in an ultrasonic bath for 20 min. Then the sample was transferred to the Cyclosizer sample container. The sample was released at maximum flow rate (≈ 14 1/min) to the cyclones during a period of time of ≈ 5 min.

Controlled elutriation was performed by subsequently reducing the water flow to ≈ 11.4 l/min and holding it constant for ≈ 20 min. Then water flow was increased and the solids collected into the apex-cones were discharged, filtered, dried and weighed.



Figure II.2. Diagrammatic arrangement of Warman Cyclosizer [114]

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II.4 X-RAY FLUORESCENCE SPECTROMETRY (XRF)

Qualitative elemental composition was determined by XRF for the original residue-samples and for the products of H_2SO_4 leaching and/or magnetic separation. The objective of the qualitative XRF was to provide a list of elements present for the search-and-match program used in X-ray diffractometry.

The XRF unit used was a Philips instrument consisting mainly of an amplifier (PW1366/60), a scaler/timer (PW1353/0), a goniometer (PW1050/25) and a fixed full-scale seconder. The radiation source was a W-tube and the unit was provided with two analyzing crystals, LiF and EDT. Also two radiation counters were available: a scintillator counter and a gas-flow proportional counter. The unit could be worked under vacuum.

In the case of the fine-powdered residue samples, they were directly briquetted at 27 kN/m² to produce a cylinder of \approx 30 mm diameter by 4 mm height. The briquettes were mounted into the XRF sample holder which was pumped down to vacuum. The sample was rotated to reduce possible errors due to sample inhomogeneity. The X-ray tube was operated at 36 kV and 20 mA. The LiF analyzer crystal and the scintillator counter were used. The goniometer angular scan was 10 to 90 (2 θ -degrees), at a speed of 2 °/min. Several scans with different recorder full-scales (between 1×10^5 and 1×10^3 counts) were performed. This method allowed the detection of major and minor elements in the sample. The LiF analyzing crystal has an interplanar distance of 0.4028 nm (4.028Å). This permitted identification of elements with atomic number larger than 19 and lower than 93. While the element spectrum is not complete, it is sufficient for the intended use of the XRF which was to provide a guide to the XRD and to the EM analyses.

II.5 ATOMIC ABSORTION SPECTROMETRY

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Quantitative analysis for Fe, Zn, Pb, Cu, As, Sn and Cd were performed using a single beam atomic absortion spectrometer IL357 (Instrumentation Laboratory). Single element hollow cathode lamps were used as light sources.

Sample preparation was dissolution of 0.2 g of sample by adding HCl and HNO₃ and heating to boiling for 10 to 15 minutes. After cooling, 50 ml of distilled water were added and the solution filtered. The filtrate was received in a 100 cm³ volumetric flask and distilled water was added to the 100 cm³ mark. From this solution aliquots were taken to dilute the solution into the linear range of absorbance vs. concentration. Three measurements with a sample time of 3 s were taken to determine the concentrations of the elements in the aliquots. Table II.2 shows the general conditions of the AA analysis for the elements of interest.

Analyzed	Detection	Wavelength	Bandpass	Gas
Element	Limit [µg/ml]	[nm]	[nm]	Mixture
As	0.4	193.7	1	Air-Acetylene
Cu	0.03	324.7	1	29 30
Fe	0.04	248.3	0.3	* *
Cd	0.01	228.8	1	**
Zn	0.008	213.9	1	77 79
РЪ	0.1	217	1	n n
Sn	1.2	23 5.5	0.5	Nitrous
				Oxide and
				Acetylene

Table II.2. Conditions of AA analysis for some elements of interest in the residues

II.6 X-RAY DIFFRACTOMETRY (XRD)

Bulk-crystallographic analysis was obtained with a vertical X-ray diffractometer coupled with an automated diffractometry software package, Philips APD 1700; version 3.0. The X-ray source was a fine-focusing Cu-tube (maximum rating 1500 W; take off angle of 6°) operated at 40 kV and 20 mA. An automatic divergence slit was used; this slit is just closed at $2\theta = 0$ and at $2\theta = 90^{\circ}$ the divergence is a maximum of 4°. This arrangement provides a constant illumination length of 12.5 mm. The automatic divergence slit gives a low background in the low angular region with good peak-to-background ratios, and high intensities at high angles [115]. A receiving slit of 0.2 mm together with a scatter slit of 1° were used in the goniometer. Monochromatic radiation was obtained by the use of a crystal monochromator (curved graphite, plane 002, radius 225 mm). The used counter was a proportional detector with sealed gas (97% Xe, 3%CO₂). The pulse high selector was set at a window of 20-80%.

The fine focusing X-ray tube used has a beam width of 0.04 mm. Therefore, the receiving slit of 0.2 mm was larger than the beam width. Although this produced a poor resolution of the $CuK_{\alpha 1}$ and $CuK_{\alpha 2}$ doublet, the $\alpha 2$ stripping did not pose special problems. This was due to the second derivative algorithm involved in the APD-peak search routine. This routine deconvolutes peaks with severe overlap [116]. On the other hand the use of a receiving slit larger than the beam width facilitated the detection of peaks due to minor phase components of the sample.

The goniometer scans used were from 5 to 100 2θ -degrees, with a step size of 0.02° and sampling times of 1 second per step.

Two methods of sample preparation were used. When enough sample was available (≈ 1.3 g), the sample was freely poured into the cavity of the standard

II ▷ EXPERIMENTAL TECHNIQUES

sample holder (an aluminum plate with a cavity of $15 \times 20 \times 1.5$ mm) and a flat surface was made by carefully pressing down the sample with a glass slide. When a limited amount of sample was available, it was sprinkled on a double-side adhesive tape, and then mounted on an empty standard sample holder. The adhesive tape used (Scotch #665) did not contribute to the XRD spectra. The latter sample preparation method is likely to produce less orientation effects. However, due to the decreased mass, less intense spectra were observed.

For all samples, other than those related to the characterization of the Cottrell dust, the search for the phases creating the XRD peaks was performed with an automated search-and-match program, SANDMAN, APD 1700 [117-119].

As mentioned, the detection of peaks is performed with a program that uses a second derivative algorithm. This means that regions of the spectra where the second derivative is negative are considered as peaks. Some inflections in the XRD spectra, due to the noise inherent in any intrument system, may fulfill the criteria of having a second negative derivative and therefore give rise to the so-called noise induced peaks. These "peaks" have nothing to do with the phases present in the samples and therefore have to be filtered out. Normally the noise induced peaks are either too broad or have almost zero peak width. These peaks are rejected in the automated XRD program by setting a minimum peak quality (MPQ) criteria that a certain peak must pass to be considered as a true XRD peak. If the MPQ is set to 1.0 then all the peaks with more than 0.01% probability of being noise induced are rejected. If the MPQ is set to 0.5 then all the peaks with more than 1% probability of being noise induced are rejected. It is clear then than an automated peak search with larger values of MPQ accepts the better defined peaks in the spectra and produces a list with fewer peaks. For the case of the identification of the major phases present it is likely that these phases create the strongest and best defined peaks. Therefore, in this thesis, the automated search match of the major phases was facilitated using K_{a2} stripped peaks with a MPQ of 1.0. Once the major

phase was determined, then more peaks with more uncertainties were allowed to pass by dropping the minimum peak quality to 0.5. The results of this peak search were corrected to match better the major phases accepted as present, then $K_{\alpha 2}$ stripped and finally used to identify the residual phases. In some cases peaks with $\approx 5\%$ probability of being noise induced were used. Peaks with more than $\approx 5\%$ probability of being noise induced were considered unreliable and therefore were never used.

To aid further the automated search-and-match of the phases, a list of elements present was provided. The source of this information was obtained by a combination of AA, XRF and SEM-EDS analysis. The qualitative analyses of the samples allowed the automated search-and-match through the JCPDS¹ data base to be performed using chemistry information and "soft" restrictions. This means that the automated search was done in three passes:

- 1.-through phases that contained any of the elements declared present and that belong to the inorganic subfile.
- 2.-through the rest of the JCPDS² subfile.
- 3.- through the rest of the "Frequently Encountered Phases" ³ subfile of the JCPDS.

It can be understood that "soft" restrictions mean that the search-and-match program might go through search passes 2 and 3 to check for phases without any of the elements declared being present. On the other hand a search with "hard" restrictions will give results considering only the pass #1. The use of "soft" restricted search-and-match avoids obvious phase missing errors that may be due to limits in the sensitivity of the qualitative methods used. In other words if

¹Joint Committee on Powder Diffraction Standards

²The inorganic JCPDS subfile (1985) contains 34925 phases

³The "Frequently Encountered Phases" subfile contains 2744 of the most common phases to find in Earth.

a phase has a very good match it could still be identified even if it does not contain any of the elements declared present [118].

For the case of the samples related to the characterisation of the copper smelter dust, (Manuscript II), the search and match for the phases present was done manually. This was simply due to the fact that the SANDMAN program was not available at the time of that work. The manual search and match was aided using likely-present compounds that were predicted from the thermodynamics involved in the process where the dusts were produced.

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II.7 THERMODYNAMIC PREDICTIONS

Thermodynamic equilibrium calculations were performed to establish which compounds may be formed at the different unit process of the copper smelting industry. The results of such calculations were used to help the identification of the X-ray diffractograms of the copper smelter dust.

In order to perform the thermodynamic equilibrium calculations, the program EQUILIB of $F^*A^*C^*T$ [140] was used. Essentially the inputs to EQUILIB are the reactants and the temperature of products and reactants; then the program gives a list of products containing all the known valid combinations of the reactants, from that list up to 20 products may be selected by the user. The selection may be done comparing the temperature of the products with the stability temperature ranges of the components in the list. Once the products are selected, the program determines the combination of the number of moles of the products that give the lowest total free energy:

$$G_{total} = \sum_{i=1}^{k} n_i G_i^{\circ} + \sum_{i=1}^{k} n_i RT \ln \left[\frac{n_i}{\sum_{i=1}^{k} n_i} \right] P$$
(II.6)

Considering only the major and medium abundant elements of the Cottrell dust (Zn, Pb, Cu, Fe, As) and the major gaseous components in copper smelting (SO₂, O₂, N₂), then it is possible to find out which compounds those elements might form that are in equilibrium at the reactor conditions. The general equation to be considered by the program EQUILIB was:

$$Zn + Pb + Cu + Fe + As + SO_2 + O_2 + N_2 = ?$$
(T, P)
(T, 1 At ...)
(II.7)

For this equation the list of the possible products contained more than 165 phases. The selection of 20 products out from 165 requires very restrictive criteria. Consequently, the reaction was submitted to EQUILIB in nine parts. This allowed a selection of (20×9) a maximum of 180 products. The reactions proposed to EQUILIB consisted of one or two metallic elements and the gaseous reactants. The computer output of EQUILIB gives the equilibrium number of moles of the gaseous phase and solid phases. An example of the output is given in Table II.3

Table II.3 shows between brackets { } the gaseous product phase. It can be seen that many species have zero moles, therefore they are not stable phases for the considered reaction. Considering the fact that the Cottrell dust is formed only by solidified phases, then the computer output for the different reactions may be simplified as in Table II.4

Different gas conditions were used in getting the stable products given in Table II.4. These conditions are typical of several unit process of copper smelting [141, 142]:

-Hearth Roasters: Produces gases with 5% SO₂ and 1% O₂.

-Fluid Bed Roasters: Produces gases with 10-15% SO₂ and 5% O₂.

Roasting Temperatures:

÷ K

-For smelting: 773-873 K

-For leaching: 950-1073 K

-Matte smelting: Produces gases with 0.5-1.5% SO₂ and PO₂ = 10^{-2} . Gas

temperatures of approximately 1523 to 1573 K.

- -Copper smelting in Blast furnace: Produces gases with SO₂=5%; at a temperature of 1673 K approximately (at tuyeres zone).
- -Copper smelting in Electric Furnace: Produces gases with 0.4 to 5% SO₂ at temperatures of 773 to 973 K.
- -Flash Furnace Matte Smelting:
 - -INCO: Produces gases with 80% SO₂ at temperatures of approximately 1523 K.
 - -Outokumpu: Produces gases with 10 to 15% SO₂.
- -Converting: Produces gases with 5 to 15% SO₂ at temperatures between 1423 to 1523 K.
- -Mitsubishi continuous copper smelting (in the smelting furnace): Produces gases with 12% SO₂ at temperatures of approximately 1473 K.

Table II.3. Example of the printout from EQUILIB

PRESS "RETURN" WHEN READY FOR OUTPUT

? ZN + 0.995*02 + 02 + N2 = (1073) (1073,0.15) (1073,0.1) (1073,0.75)

1.324

(+ + + + + + + +	.755 .139 .734E-01 .320E-01 .120E-11 .207E-22 .947E-27 .542E-27	N2 S*02 O2 S*03 ZN S20 S2 ZN*S	}
		(1073.0, 1.00	,G)
+	.237	ZN*O(ZN*S*O4)2 (1073.0, 1.00	,51)
+	.0	ZN*S*04 (1073.0, 1.00	,51)
+	.290	ZN*S*04 (1073.0, 1.00	,52)
+	.0	ZN*S (1073.0, 1.00	,51)
+	.0	ZN*S (1073.0, 1.00	, S2)
+	.0	ZN*O (1073.0, 1.00	,51)
+	.0	ZN3N2 (1073.0, 1.00	,51)
+	.0	ZN (1073.0, 1.00	,51)
+	.0	S (1073.0, 1.00	,51)
+	.0	S (1073.0, 1.00	,52)

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REA	CTAN	TS AND) THEI	R CONDITIONS		EQ	UILIBRIUM PR	ODUCTS	;
Т	Zn.	PSO ₂	PO ₂	PN ₂		TPROD	$2nO(2nSO_4)_2$	ZnSO ₄	ZnO
	L	G	G	G	=		S 1	S1	S1
773	1.0	0.05	0.1	0.85	=	773	0.01	0.97	0
873	1.0	0.05	0.1	0.85	=	873	0.01	0.97	0
								S2	
1073	1.0	0.05	0.1	0.85	=	1073	0.237	0.290	0
								S 1	
773	1.0	0.15	0.1	0.75	1	773	0.01	0.97	0
873	1.0	0.15	0.1	0.75	=	873	0.01	0.97	0
								S2	
1073	1.0	0.15	0.1	0.75	=	1073	0.237	0.290	0
	G								
1523	1.0	0.05	0.01	0.94	#	1523	0	0	1.0
1573	1.0	0.05	0.01	0.94	=	1573	0	0	1.0
1673	1.0	0.05	0.1	0.85	=	1673	0	0	0.99
1423	1.0	0.1	0.1	0.8		1423	0	0	1.0
1523	1.0	0.8	0.1	0.1	=	1523	0	0	1.0
1423	1.0	0.15	0.1	0.8	=	1423	0	0	1.0
1523	1.0	0.15	0.1	0.75	=	1523	0	0	1.0

Table II.4. Simplification of output from EQUILIB

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Table II.4 continues ...

REAC	TAN'	rs and	THEIR	CONDITIONS		1	EQUILI	BRIUM PI	RODUCTS		
T	РЬ	PSO ₂	PO ₂	PN ₂		TPROD	PbO.PbSO4	PbSO4	(PbO) ₄ PbSO ₄	PbS	
	L	G	G	G	=		S 1	S1	S1	S1	
773	1	.05	.1	.85	=	773	0.01	0.98	0	0	
773	1	.05	.01	.85	1 =	773	0.01	0.98	0	0	
773	1	.05	.01	.85	=	1073	.0102	.979	0	0	
873	1	.05	.1	.85	=	873	.01	.98	0	0	
873	1	.05	.1	.85	=	1523	0	0	.168	0	
873	1	.05	.1	.85	=	1573	0	0	0.120	0	
1073	1	.05	.01	.85	=	1073	.01	.979	0	0	
1623	1	.05	.1	.85	łł	1623	0	0	0.168	0	
1673	1	.05	.1	.85	=	1573	0	0	0.120	0	
1523	1	.08	.1	.1	=	1523	0	0	0.168	0	
1423	1	.1	.1	.8	=	1423	0	0	0.490	0	
873	1	.1	.05	.85	=	1673	0	0	0	0+++	
	$+++0.85(PbO) + 0.7(SO_2) + 0.35(O_2) + 0.070(Pb) + 0.07(SO_2)$										
1	THE PREVIOUS PRODUCTS WHEN COOLED DOWN TO ROOM TEMPERATURE WILL GIVE:										
					=	298	.150	.602	0	.017	

Table II.4 continues ...

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REAC	JTAN	TS AND	THE	R CONDITIONS		EQUILIBRIUM PRODUCTS				
T	C	PSO ₂	PO ₂	PN ₂		TPROD	CuOCuSO4	CuSO ₄	Cu ₂ O	
	8	G	G	G	#		S 1	S 1	S 1	
773	1	0.05	0.1	0.85	=	773	0.01	0.98	0	
873	1	0.1	0.1	0.8	=	873	0.01	0.975	0	
873	1	0.1	0.1	0.8	=	1073	0.5	0	0	
	L									
1523	1	.05	0.1	0.85	=	1523	0	0	0.5	
	S									
873	1	0.1	0.1	0.8	=	1573	0	0	0.5	
873	1	0.1	0.1	0.8	=	1673	0	0	0.5	
	L									
1523	1	0.8	0.1	0.1	=	1523	0	0	0.5	
	S									
873	1	0.1	0.1	0.8	=	1423	0	0	0.5	

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Table II.4 continues ...

REAC	TAN	TS ANI) THE	R CONDITIONS		EQU	JILIBRIUM	PRODUC	TS
T	Fe	PSO ₂	PO ₂	PN ₂		TPROD	Fe2(SO4)3	Fe ₂ O ₃	Fe ₃ O ₄
1	S1	G	G	G	=		S 1	S1	S 1
773	1	0.05	0.01	0.94	=	773	0.166	0.334	0
873	1	0.05	0.1	0.85	=	873	0.166	0.334	0
873	1	0.05	0.1	0.85	=	1073	0	0.5	0
773	1	0.05	0.01	0.94	=	1523	0	0	0.333
873	1	0.05	0.1	0.85	=	1573	0	0	0.333
873	1	0.05	0.1	0.85	#	1673	0	0	0.333
	S2								
1523	1	0.8	0.1	0.1	=	1523	0	0	0.333
	S 1								
873	1	0.05	0.1	0.85	=	1423	0	0.5	0

Table II.4 continues ...

REAC	TAN	TS ANI) THE	R CONDITIONS		EQUILIBRIUM PRODUCTS				
T	As	PSO ₂	PO ₂	PN ₂		TPROD	As205	A4203		
	S	G	G	G	=		S 1	S1		
773	1	0.05	0.1	0.85	=	773	0.208	0.2925		
873	1	0.1	0.1	0.8	=	873	0.151	0.349		
873	1	0.1	0.1	0.8	=	1073	0	0.5		
773	1	0.05	0.1	0.85	=	1523	0	0.5		
873	1	0.1	0.1	0.8	Ħ	1573	0	0.5		
873	1	0.1	0.1	0.8	=	1673	0	0.5		
	G									
1523	1	0.8	0.1	0.1	=	1523	0	0.5		
873	1	0.1	0.1	0.8	=	1423	0	0.5		

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REACTANTS AND THEIR CONDITIONS EQUILIBRIUM PRODUCTS							S				
T	As	Cu	PSO ₂	PO ₂	PN ₂		TPROD	As203	Cu ₂ O	Cu ₃ As	CuSO ₄
	S	S	G	G	G	=		L1	S1	S1	S1
773	1	1	0.05	0.1	0.85	=	773	0.5	0.5	0	0
	G	S	•			=		S 1			
1073	1	1	0.05	0.1	0.85	=	298	0.401	0	0.198	0.405
	S					Ħ		L1			
773	1	1	0.05	0.1	0.85	=	1573	0.5	0.499	0.0008	0
						=					
773	1	1	0.05	0.1	0.85	=	1673	0.499	0.497	0.0021	0
	G	L				=		S 1			
1673	1	1	0.05	0.1	0.85	H	298	0.401	0	0.198	0.405

Table II.4 continues ...

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REAC	CTAN	TS A	ND TH	EIR CO	NDITIONS		E	QUILIBR	IUM PF	ODUCT	S
T	Zn	As	PSO ₂	PO ₂	PN ₂		TPROD	A\$203	ZnO	Zn ₃ As	ZnSO ₄
	L	S	G	G	G	II		S1	S1		
773	1	1	0.05	0.1	0.85	=	773	0.5	1.0	0	0
773	1	1	0.05	0.1	0.85	I	873	0.5	1.0	0	0
		G				=					S1
1073	1	1	0.05	0.1	0.85	=	298	0.5	0.507	0	0.493
		S				=			1		
773	1	1	0.05	0.1	0.85	=	1073	0.499	1.0	0	0
773	1	1	0.05	0.1	0.85	=	1523	0.464	0.911	0	0
773	1	1	0.05	0.1	0.85	=	1673	0.488	0.591	0	0

Table	II.4	continues	•••

REACTANTS AND THEIR CONDITIONS					EQUILIBRIUM PRODUCTS					
T	Zn	Fe	PSO ₂	PO ₂	PN ₂		TPROD	$ZnOFe_2O_3$	$ZnO(ZnSO_4)_2$	Fe_2O_3
773	1	1	0.05	0.1	.085	Ħ	298	0.260	0.247	0.240
1073	1	1	0.05	0.1	0.85	=	298	0.260	0.247	0.240

Table II.4 continues ...

REACTANTS AND THEIR CONDITIONS							EQUILIBRIUM PRODUCTS				
T	Cu	Fe	PSO ₂	PO ₂	PN ₂		TPROD	Cu ₅ FeS ₄	Cu ₂ OFe ₂ O ₃	CuSO ₄	Fe ₂ (SO ₄) ₃
773	S 1 L	S1 1 S3	G .05	G .1	G .85		298	S3 0.066	S2 0.269	S1 0.132	51 0 198
1673	1	1	.05	1	.85	=	298	0.066	0.269	0.132	0.198

Table II.4 END

Table II.4 shows that the main variable is temperature; with this in mind the processes may be broadly divided into low temperature processes (up to 1073 K, e.g. Roasting) and high temperature processes (up to 1573 K, e.g. Smelting and

Converting). With this division, Tables II.5 and II.6 present the thermodynamically probable compounds in the dust.

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The Cottrell dust obtained from Kidd Creek comes mainly from the Mitsubishi Smelting reactor. In this reactor the temperature is around 1473 K and SO₂ around 12%, therefore, Table II.6 gives the probable compounds to be found in the dust sample. These compounds were used to help in the identification of the phases producing the XRD patterns of the samples related to the characterization of the Cottrell dust.

II ▷ EXPERIMENTAL TECHNIQUES

	MAJOR	MEDIUM	MINOR
ZINC as	ZnSO ₄	$ZnO.(ZnSO_4)_2$	
		ZnO	
		ZnO.Fe ₂ O ₃	
LEAD as	PbSO4		PbO.PbSO ₄
COPPER as	CuSO ₄	Cu ₂ 0	Cu ₅ FeS ₄
		CuO.CuSO ₄	
		Cu ₂ 0.Fe ₂ O ₃	
IRON as	Fe ₂ O ₃	$Fe_2(SO_4)_3$	Cu ₅ FeS ₄
		$ZnO.Fe_2O_3$	
		$Cu_2O.Fe_2O_3$	
ARSENIC as	As ₂ O ₃	As ₂ O ₅	

Table II.5. Thermodynamic Stable Compounds in the dust corning from Roasters.

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Table	II.6 .	Thermo	dynami	c Stable	Cor	npounds	in	the	dust	coming
fr	om S	melting	and Cor	nverting	and	Continue	DUS	Pro	cesses	L

	MAJOR	MEDIUM	MINOR
ZINC as	ZnO	ZnO.Fe ₂ O ₃	$ZnO(ZnSO_4)_2$
LEAD as	PbSO4	(PbO)4.PbSO4	
COPPER as	Cu ₂ O	Cu ₂ O.Fe ₂ O ₃	Cu3As
			Cu ₅ FeS ₄
			CuSO ₄
IRON as	Fe ₃ O ₄	Fe ₂ O ₃	Cu ₅ FeS ₄
		$Cu_2O.Fe_2O_3$	$Fe_2(SO_4)_3$
ARSENIC as	As ₂ O ₃		Cu ₃ As

II.8 ELECTRON MICROSCOPY

Electron Microscopy was performed with two different instrumental set-ups:

- JEOL-SEM model T300 coupled with a Tracor analyzer.
- JEOL-TEM model 100CX with STEM capabilities coupled with a Princeton Gamma-Tech. analyzer (PGT-4).

The Tracor analyzer used with the T300 SEM was updated several times during the course of this investigations. The following systems were used: TN880; TN5500; and TN5400-TN5700. All the systems permitted standard EDS analysis; i.e. acquisition of an EDS spectra, setting of regions of interest within the EDS spectra and manipulation of those regions to produce element maps or line analysis, etc. The systems TN5500 and TN5400-TN5700 also incorporated automated image analysis.

The STEM set-up was used when the particle size in the samples of interest necessitated magnifications between ≈ 35000 to $\approx 100,000X$. The PGT-4 analyzer also allowed all the standard capabilities of EDS systems.

EM-EDS methods were most often used for characterization of the particles present in the different samples. Less frequently, the SEM-EDS set up (JEOL T300) was used for bulk chemical analysis. This was done only when the amount of sample precluded or made difficult the bulk chemical analysis by other methods (AA, XRF, etc). The bulk chemical analyses performed with SEM-EDS were used only as guides for the computer search-and-match in XRD analysis. Performing bulk chemical analysis by SEM-EDS necessitates the use of very low magnifications. Consequently the experimental EM procedure is divided in two parts: low magnification SEM-EDS and high magnification EM.

II.8.1 Low magnification SEM-EDS

SEM-EDS techniques were applied to the task of obtaining a bulk chemical analysis. For this very low magnifications were used on heavily loaded sample holders. The analyses were, of course, considered only as guidelines and were performed only when the amount of sample was limited.

The samples were sprinkled on a double-sided adhesive tape, providing a dense coverage. The tape was then mounted on a spectroscopically pure graphite stub (standard pin-type or planchets). There are a number of double-adhesive tapes commercially available. Witcomb [121] has tested several double-sided adhesive tapes for SEM work. From his results the Scotch double coated tape #665 was selected because it shows a simple composition and gives very small EDS-K_a peaks due only to silicon and chlorine. The ratio of the peak to background was only 0.2 for both elements and would not represent an interference problem in analysis. Other workers [122-124] have also found tape #665 satisfactory.

Once the double-adhesive tape with the sample was mounted on the graphite stub, the edge was painted with carbon conductive paint to enhance conductivity from the specimen to the stub [122]. The sample on the graphite stub was also carbon coated by thermal evaporation to reduce charging phenomena in the SEM. The samples could be C-coated without cracking or contraction of the tape only when large vacuum bells were used. Two evaporator set-ups could be used without tape damage:

1.- A Polaron vacuum thermoevaporator model E642 fitted with a bell jar of ≈ 24 cm diameter by 30 cm length. The sample stage was rotated continuously at $\approx 6-8$ r.p.m. during evaporation, and the evaporation pressure was 2×10^{-3} Torrs. The distance between the electrodes and the sample stage

was ≈ 9 cm, and the angle between the normal to the specimen and the evaporation direction was $\approx 19^{\circ}$.

2.- A Denton vacuum thermoevaporator model DV-502 fitted with a bell jar of ≈ 25 cm diameter by 40 cm length. The sample stage was rotated continuously at ≈ 8 r.p.m, the bell pressure was 2×10^{-4} Torrs. The distance between the electrodes and the sample stage was ≈ 10 cm and the angle $\approx 29^{\circ}$.

In contrast, tape damage occurred when C-coating was done with a Hummer VI sputtering system. This unit has a carbon-evaporation attachment. The bell jar of this unit is ≈ 10 cm diameter by 15.5 cm length. The carbon electrodes are directly over a stationary sample stage at a distance of ≈ 9 cm. For C-evaporation, normally the unit is pumped down as low as possible (around 1.0×10^{-2} Torrs) and pressurized argon is added to give a total pressure of 1.0×10^{-1} Torr.

The tape damage occurring during C-coating with the Hummer VI system could be due not only to the smaller bell jar used, but also to the higher temperature required for C-evaporation at higher pressures. It should be noted that no tape damage was observed if the Hummer VI system was used in the sputtering mode (with a Pt-Au target). In this case the unit has a planar magnetron triode configuration that allows samples to be coated without thermal damaging effects. However this configuration was not used because of the higher possibility of overlaps in EDS analysis with the several peaks that gold shows.

The samples thus prepared were analyzed by SEM-EDS. The heavy coverage of the sample on the tape was evident in the SEM by a high particle overlapping. This does not provide good microanalysis conditions. However the purpose of these samples was to obtain a fast, qualitative, bulk analysis. The EDS spectra were acquired using a chisel nose Si-Li detector with a 7.5 μ m thickness Be window, a detector horizontal position to pole center line of 10 mm, a working distance of 25 mm, with a zero sample tilt, a take-off angle between 36° to 53° and the max-

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imum SEM-accelerating voltage of 30 keV (JEOL-SEM T300) and magnifications lower than 100X. The X-ray count rate at these conditions was \approx 5000 counts/s. The use of low magnifications and heavy sample coverage permitted bulk qualitative analysis results to be obtained from a technique that is normally applied for microanalysis. The maximum accelerating voltage was used to increase detection limits on the heavier elements where only the weaker L and M emission lines were available. It is recognized that the use of high accelerating voltages involves a higher absortion in the sample due to an increase of the depth of X-ray production, R (R is a function of the accelerating voltage, the density of the sample and its critical ionization energy; for example at 30 keV, for pure silicon, R=8.2 μ m and for pure zinc R=2.3 μ m [125,126]). However, for the particular case, a large depth of penetration will yield better results for bulk qualitative analysis.

The EDS spectra were treated with a standardless quantitative program (SQ, Tracor, TN5500). However the results of this program were considered, in this instance, only as semi-quantitative and were used only to give an idea of the relative concentration of the elements present.

EDS with Si-Li detector and a Be window can detect [127] elements with atomic numbers larger than 11 (sodium). In this sense the bulk qualitative analysis could be considered incomplete. However for the intended use of the results this was not crucial (see section II.6 XRD, also ref. 118).

II.8.2 Sample preparation for High-magnification EM

The sizes of the particles present in the residues indicate the need to use electron microscopy to obtain morphology, chemistry and particle-to-particle association data on these materials. Electron microscopy of fine particle samples is best if the particles are well dispersed. Adequate dispersion of the sample is necessary to know if particles of different compositions are intrinsically bonded or are simply in close juxtaposition due to an improper preparation technique.

The first sample to be studied by EM was the Cottrell dust of the Kidd Creek copper smelter. The particle size analysis of this sample by Cyclosizer gave 88% finer than 8 μ m and only 3% was between 27 and 20 μ m. Particles of this size are susceptible to electrostatic attraction. Therefore dry mounting on a double-sided adhesive tape or even air dispersion did not provide an adequate dispersion. Figure II.3 illustrates the Cottrell dust slightly sprinkled on a double-sided tape; poor dispersion is evident. For such situations liquid dispersion is recommended [81, 128].

The optimum liquid-dispersion technique was selected by trying several techniques and dispersion media. The quality of dispersion was evaluated by simple observation in scanning and/or transmission mode with the STEM (JEOL 100CX). For this, the dispersion media was filtered on a Nucleopore membrane filter of 47 mm in diameter and pores of 0.2 μ m. The membrane was C-coated using the same methods and precautions as those described in section II.8.1. At the same time the Jaffe Wick apparatus was prepared. This consisted of a glass Petri dish where a stack of filter paper is placed and soaked with chloroform. 200-mesh electron microscope grids were placed on top of the paper-stack. A section of the C-coated membrane was then cut and placed on top of the grid. Then the Petri dish was closed and allowed to stand overnight. This caused dissolution of the backing filter by the cholorofrn leaving the particles supported by a carbon film. Finally the grids were observed in the STEM and quality of dispersion evaluated.

Several membrane filters are commercially available, the most common being: Millipore, Gelman, Nucleopore, Uni-pore, and Flotronics. Murphy [123] and Rostgaard and Christensen [129] give information on membrane filters for EM purposes. Nucleopore was selected because its lack of surface structure causes less particle loss in the filter matrix [130]. EM grids are available in several mesh sizes; however, the 200-mesh size was selected because it provides a good compromise between open area and support [131]. Care was taken to use the bright side of the grids to place the membrane sections. This was because the bright size is smoother and permits better thermal and electrical contact with the specimen [131]. The dispersion studies were all done using gold or copper EM grids. However, once the dispersion technique was established, titanium grids were used. These grids have the advantage of producing simple EDS spectra that do not overlap with the peaks of the elements present in the sample.

It should be noted than the same membrane filter with C-coating could be mounted on a graphite stub for normal Scanning Electron Microscopy (JEOL-SEM T300).

The first dispersion technique tried was using water as the dispersion media. For this a known amount of solids were added to 100 cm^3 of water in a beaker. Then the beaker was placed in an ultrasonic bath with water and left there for 1 hour. The 100 cm³ were then filtered in the Nucleopore membrane. Table II.7 shows the first test series.



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Figure II.3. Backscatter image of poorly dispersed dust showing particle overlap

			SOL CONCEN	IDS FRATION
CODE			C _L	C _N
SOLID	AMOUNT	AMOUNT		
LIQUID	OF	OF	IN S/L	ON
(S/L)	WATER	SOLIDS	MIXTURE	FILTER
MIXTURE				
	[cm ³]	[g]	[g/cm ³]	$[g/cm^2]$
SO1	100	0.0418	4.18×10 ⁻⁴	2.41×10^{-3}
SO2	100	0.0340	3.40×10 ⁻⁴	1.96×10 ⁻³
SO6	100	0.0257	2.57×10^{-4}	1.48×10^{-3}
SO3	100	0.0177	1.77×10 ⁻⁴	1.02×10 ⁻³
SO4	100	0.0082	8.20×10^{-5}	4.73×10 ⁻⁴
SO5	100	0.0056	5.60×10^{-5}	3.23×10 ⁻⁴

Table II.7. First Dispersion Series. Water used as dispersion media, 1 hr. in ultrasonic bath and filtration on Nucleopore 0.2 μ m.

From geometric considerations, it is possible to calculate the distance between particles in the solid-liquid mixture. Some simplifying assumption are required for this calculation, namely:

- 1.- The particles are perfect spheres.
- 2.- The particles are as far apart as possible and the inter-particle distance is constant.
- 3.- All the particles have the same size and same density.

Using these assumptions the following can be derived:

1.- The total volume of the particles (V_P) per unit volume in the solid/liquid mixture is:

$$V_{P} = \frac{4}{3} \pi a^{3} n_{0} = \frac{cm^{3} \text{ of particles}}{cm^{3} \text{ of liquid}}$$
(II.8)

where:

a = particle radius [cm]

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The volume V_P can be also obtained by:

$$V_P = \frac{C_L}{\delta_P} = \frac{cm^3 \text{ of particles}}{cm^3 \text{ of liquid}}$$
(II.9)

where:

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$$C_L$$
 = concentration of solids per unit
volume of mixture in g/cm^3 (see Table II.7)
 δ_P = density of the particles in g/cm^3

Combining eqs II.8 and II.9 the number of particles per unit of volume can be obtained:

$$n_0 = \frac{C_L}{(4/3)\pi a^3 \delta_P}$$
(II.10)

2.- The considered volume of suspension (V) is unitary, i.e. one cubic centimeter.

This is also equal to:

$$V = \frac{4}{3}\pi R^3 n_0 = 1 \qquad (II.11)$$

where:

R = distance between centres of particles [cm]

R can be obtained substituting II.10 in II.11:

$$R = \left[\frac{a^3 \,\delta_P}{C_L}\right]^{\frac{1}{3}} \tag{II.12}$$

3.- The distance (d, in cm) between particles is:

$$d = R - 2a \tag{II.13}$$

II > EXPERIMENTAL TECHNIQUES

or, substituting II.12 in II.13:

$$d = \left[\frac{a^3 \,\delta_P}{C_L}\right]^{\frac{1}{4}} - 2a \qquad (II.14)$$

To apply equation II.14 to the dispersions of Table II.7, the values of "a" and " δ_p " for the Cottreli dust must be known or estimated. The Cyclosizer size analysis showed the dust to contain 88% (wt) finer than 8 μ m; and the bulk density of the dust was determined as 4.5 g/cm³. Table II.8 shows the calculated values for the distance (d) between particles in the liquid suspension. The values were obtained assuming that all the particles have a value of $\delta_p=4.5$ and that the particle size could be considered as 3 μ m. It can be seen that all the solid/liquid mixtures have large inter-particle distances (d). Therefore it is possible to consider the particles well dispersed in the solid/liquid mixture (even if one considers particle collisions due to perikinetic or orthokinetic coagulation).

The STEM observations of the samples showed no particle dispersion. This is not surprising since all the 100 cm³ of the solid/liquid mixture were filtered. Therefore even if the particles were dispersed in the liquid, then on top of the Nucleopore membrane they were not. This can be shown using geometric equations similar to those of equations II.8 to II.14, but applied to dispersion on an area:

$$d_N = \sqrt{\frac{(4.7/2)^2}{100 n_0}} - 2a \qquad (II.15)$$

where:

 d_N = distance between particles on the filter (cm)

$$4.7 = \text{diameter (in } cm) \text{ of the filter}$$

 n_0 = number of particles per cm³ in the solid/liquid mixture

$$a = particle size (cm)$$

II ▷ EXPERIMENTAL TECHNIQUES

Table II.8 shows that d_N is a negative value for all the dispersions except SO5. Negative values for d_N means lack of dispersion. In the STEM observations even the SO5 showed poor dispersion. This is understandable since d_N was calculated for a perfect planar distribution of particles. This is not the real case. The value of d_N for the dispersion SO5 is only 1 μ m, this is a value too low to indicate a good practical dispersion.

CODE	SOLIDS CO	NCENTRATION	DISTANCE	BETWEEN
FOR			PART	ICLES
SOLID-	IN THE	ON THE	IN THE	ON THE
LIQUID	S/L	FILTER	S/L	FILTER
MIXTURE	MIXTURE		MIXTURE	
	C _L	C _N	d_L	\mathbf{d}_{N}
	$[g/cm^3]$	$[g/cm^2]$	[µm]	[µm]
SO1	4.18×10 ⁻⁴	2.41×10 ⁻³	60	negative
SO2	3.40×10 ⁻⁴	1.96 ×10 ⁻³	65	negative
SO6	2.57×10^{-4}	1.48×10 ⁻³	72	negative
SO3	1.77×10^{-4}	1.02×10 ⁻³	82	negative
SO4	8.20×10 ⁻⁵	4.73×10 ⁻⁴	108	negative
SO5	5.60×10 ⁻⁵	3.23×10 ⁻⁴	124	1.08

Table II.8. Inter-particle distances in the solid/liquid mixtures and on the Nucleopore membrane filter.

The aforementioned shows that in order to have a good dispersion of particles in the sample for EM it is necessary to consider two factors, 1.- good particle dispersion in the solid/liquid mixture and 2.- good particle dispersion on the membrane filter. The next tests were planned such that 1/5 and 1/10 of C_N for SO5 could be obtained. This would give d_N values of 4 and 17 μ m respectively.

Figure II.4 shows the sample dispersion method followed for these two tests. The method was developed to avoid sampling problems. The first hydrosol allows the use of an acceptably large solid sample. In general sampling of liquids is easier than sampling of solids. Therefore the first hydrosol allows preparation of a second

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hydrosol which is more diluted in solids and therefore permits use of an acceptably large volume for filtration.

The STEM observations showed that sample dispersion was relatively better for test $\frac{1}{10}C_{Nsos}$ than for any other previous test. However dispersion was still unsatisfactory. Therefore other dispersion test were planned.





Table II.9 gives a brief description of all the dispersion tests. The effect of the liquid media on the solid particle dispersion was studied. Literature showed that methanol [81, 128, 132] and 2-propanol [81] have been used for dispersion of other fine-particle solids. Two pH levels were also tried (basic ≈ 11.5 and acid ≈ 2.5) to
determine the general effect of this variable. Besides filtration on Nucleopore, two other mounting methods were tried: spraying [132, 133] the solid/liquid mixture on Nucleopore and placing drops with a micropipette on a C-coated EM grid [122, 123, 133].

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In the end, water dispersion methods were abandoned because it was found that the sample had some water-soluble components. The method that gave adequate particle dispersion for EM studies was that of test T14, dispersion in propanol followed by filtration on Nucleopore. Besides it was found that the sampler of this study had negligible solubility in propanol. The details of this dispersion method are given in Figure II.5. Figure II.6 shows the quality of particle separation obtained with the sample dispersion method of Figure II.5. Hence the sample preparation method depicted in Figure II.5 was adopted to prepare most of the samples for EM studies.

Not all the sample fractions studied by SEM required the sample dispersion method of Figure II.5. Some of the fractions had coarse particle sizes. For example all the fractions derived from the Cyclosizer cone 3 size ($\approx 19 \ \mu m$). These samples were directly and lightly sprinkled on double-side adhesive tape(Scotch #665). These tapes were C-coated as described in section II.8.1



Figure II.5. Final method for sample preparation for E-M



Figure II.6. Particle dispersion obtained using 2-Propanol with solid concentration of 1.0×10^{-4} g/cm³ providing a solid concentration on the membrane of 3.0×10^{-5} g/cm².

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TEST	L	V	C _L	OT	5	рн	VHI	V -	CL	OT	-3	рН			OTHER	C _N
CODE			×10 ³		l				×10-3							× 10-8
\$01	WATER	100	41.8	•		NATURAL							Y			241
502			84.0	-												196
506	•	•	28.7		•	•										148
508			17.7	•												102
504			8.2	•												47.3
305			5.6	•	•	•										32.8
CNSOS	•	250	107.8	0.2	•		10.4	100	11.2	0.1	1 h	NATURAL	•			16.8
TACNSOS	•	•	*	•	•	•	•	•	٠	•		٠	•			8.23
T 1				•			•	35	9.8	0.1		11.6 with NH_OH				1.61
T 2						• • • •						2,4 with HCl				
TS	•		•		•	•	10	\$ 0	21.6	1		11.5 with NH ₄ OH	N	Y		0.61
74										1		2.7 with HCi				0.61
76	METHANOL	100					10.4	100	11.2	1 .		NATURAL	Y	N		3.23
76				1			17.8	80	87.8	1		•	Ř	ΤŶ-		0.61
77		•	•	-			10.4	100	11.2	·		2.5 with HCl	Y	N		3.23
78							17.8	50	87.8	+			N	TY I		0.61
79				•			10.4	100	11.2	- 1		11.8 with	Y	R		3.28
T10				<u> </u>	1	† • • • • • • • • • •	17.8	80	\$7.8	1			N	Y		0.61
Ť11	WATER			0.2		·	5	55	9.8	0.1			Y	N		3.22
T 12													N	N	a 2 mml drop was placed on an EM grid coated with C	≈3.22
T18			1	1									M	I Y		8.22
T14	PROPANOL	60	124	-			1 5	50	12	· ·		NATURAL	ЦY	I N		3.22

Table II.9. SUMMARY OF DISPERSION TESTS

TABLE CODES

H1 = Piret solid/liquid (S/L) mixture

H2 = Second \$/L misture

L = Type of liquid modia

V = Total volume of solid/liquid mixture [cm³]

OL = Concentration of solids in the S/L mixture [g of solids/cm³ of liquid]

OT = % volume of Surfactant OT

5 = Period of time [hro] in an ultraconic bath

pH = pH of the S/L mixture

VH1 = Volume of H1 used to prepare H2 [cm²]

 $P = Piltration on a 0.3 \mu m Nucleopere membrane; yes or no option (Y/N)$

A = Aspiration (Sprayed with a gas-propellent bottle) on a 0.2 μ m Nucleopore (Y/N)

C_N = Concentration of solids on Nucleopore [g of solids/cm² of membrane]

II.9 FRANTZ ISODYNAMIC MAGNETIC SEPARATOR

This laboratory device is best known for its geological and mineralogical application in achieving precise separations of minerals of different magnetic susceptibilities [109]. It has also been used to provide an indication of the amenability of a mineral mixture to processing by magnetic methods in general [134] and by HGMS in particular [104, 105, 108]. Figure II.7 shows a photograph of the Frantz and a schematic view of it.

The separation of particles occurs in a tray positioned lengthwise in the gap (approximately 25 cm long) between specially designed pole pieces of a powerful electromagnet. The cross-section of these "isodynamic" poles is such that the changing field gradient exactly balances changes in the magnetic field to yield a uniform magnetic force throughout the gap. Since gravity, the only opposing force (adjusted by changing the side slope of the device) also remains constant, a separation of particles is achieved which is totally independent of their mass and solely a function of individual magnetic susceptibility. In despite of the later, all the Frantz magnetic separations performed for the present experimental work were done using the cone 3 fraction of the Cyclosizer. The use of a relatively coarse fraction ($\approx 19 \ \mu$ m) allowed the magnetic separation to be performed reasonably easily because electrostatic particle agglomeration is decreased on coarse particles and because mechanical misplacement is reduced. The longitudinal variation of the magnetic field (H) in the pole gap appears in Figure II.8 [136]. It shows that the particles enter and exit under essentially zero field conditions, while being exposed to a constant H (longitudinally) in the separation zone. At the end of the separation zone a splitter in the tray parts the feed into magnetic and non-magnetic fractions. Beyond this splitter location the field smoothly and rapidly decreases allowing for continuous removal of both products.

An indication of the transverse variation in the magnetic field appears in Figure II.9 [136]. It can be seen that the location of the maximum field occurs slightly to the outside of the separation tray. Therefore the magnetics are pulled towards that side.

The Frantz magnetic separations consisted in fractionating the sample into magnetics and non-magnetics at a given current [mA] to the magnet coils. The sample was fed slowly and evenly by a vibrator to approach separation on a particleby-particle basis. Typically the feed rate was such, that a 1-gram sample took 3-days to process. When all the sample was passed, the magnetics were weighed and stored while the non-magnetics were used as feed for a higher current setting.

Table II.10 shows the correspondence between the current in milliamperes and the magnetic field in Tesla (T). The values in Table II.10 were obtained following the calibration procedure described elsewhere [108, 136].





Figure II.7. a) General view of the Frantz isodynamic separator. b) Schematic [135] of the Frantz. Fg=gravity force; Fm=magneticforce; $\theta 1=$ forward slope; $\theta 2=$ side slope (20° respectively for all the tests performed in the experimental work for this thesis







Figure II.9. Transverse variation in field H in the pole gap of the Frantz separator. Measurements taken at longitudinal station #2 (1 station equals 2.54 cm)

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Current	Field
[mA]	[T]
25	0.04
50	0.07
100	0.13
200	0.2675
500	0.68
750	1.0
1000	1.325
1250	1.625
1500	1.875
1750	2.0

 Table II.10. Calibration of the Frantz magnetic separator showing the correspondence between current and magnetic field

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II.10 High Gradient Magnetic Separation (HGMS)

HGMS tests were performed on the Cottrell dust, the jarosite and hot-acid leach residues.

The HGMS separator is a device in which the magnetic field and process flow rate are controlled and particles are trapped on an array of wires (matrix). Depending on the orientation of field, flow and wires, HGMS can be further subdivided. One arrangement is field and flow parallel and at right angles to the wires (longitudinal HGMS). The matrix was an array of discs or sheets cut from expanded metal and arranged verically. A vertical array reduces non-magnetic entrapment between the dics and allows passage of the small fraction of larger particles [138]

The HGMS apparatus used was an Eriez Magnetic model EL5-4. The unit consists of mild steel plates bolted together to form a box 635 mm square and approximately 229 mm deep. The energizing coil is completely enclosed in the steel box. In turn, the coil encloses a Plexiglas container with the matrix through which the slurry is passed. The coil is coupled with a D.C. Power supply unit input of 480 Volts, 3-PH, 60 Hz and a dual output of 1000 Amp, at 125 Volts D.C. or 500 Amp at 250 Volts D.C. The magnetic filed intensity of the Eriez EL5-4 unit is variable up to 2 Tesla (20,000 Gauss).

The matrix in the Plexiglas was built of 28 expanded metal sheets, with diamond-shaped holes (4 x 8 mm) and wires with diamond cross-section with an hydraulic diameter of 0.5 mm. The metal sheets were held in vertical array separated by 1.5 mm aluminum spacers. The matrix was 6 cm long by 4x4.5 cm square with a mass of 46.6 g.

Figure II.10 shows a schematic view of the apparatus set-up. The plumbing was constructed from a copper tubing with an internal diameter of 1.5 cm. Feed

from a stirrer tank is introduced via a constant head tank. Flow rate is controlled by calibrated bore brass plugs in the discharge line. A back-flush line is available for matrix flushing. The samples to be tested were previously dispersed in water with 0.1-0.2% Calgon solution followed by 30 minutes of ultrasonic agitation.



Figure II.10. Schematic view of the HGMS set-up

SECTION III

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MANUSCRIPTS PUBLISHED

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LEARNED JOURNALS

Connecting Text for Manuscript I: Characterization of Metallurgical Residues by Electron Microscopy

The first metallurgical residue to be characterized in the experimental part of this thesis was the Cottrell dust of the Kidd Creek Mitsubishi Copper Smelter. The particle analysis of this residue showed 88 % finer than 8 μ m with only 3 % between 27 and 20 μ m. Consequently, electron microscopy was selected to study the morphology, chemistry and particle-to-particle associations in this residue. However simple sprinkling or even air dispersion to mount the powders on SEM stubs proved to be unacceptable due to agglomeration of particles. Adequate dispersion of the sample is necessary to determine if particles of different compositions are intrinsically bound or are simply in close juxtaposition due to the sample preparation technique.

The following paper explains briefly the sample preparation technique followed to perform EM studies of fine-particle residues. The paper also reveals the power of electron microscopy for providing information on morphology and chemistry on a particle-to-particle basis. The paper presents and discusses briefly some of the results obtained on the residues.

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MANUSCRIPT I

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Characterization of Metallurgical

Residues by Electron Microscopy

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CHARACTERIZATION OF METALLURGICAL RESIDUES BY ELECTRON MICROSCOPY

N. Rowlands and R. Lastra

Metallurgical residues are commonly thought of as slags associated with ferrous and non-ferrous smelting. However, these residues may also manifest themselves in fine-grained particulate forms such as precipitator dusts from stacks and as finely disseminated waste products from electrolytic or hydrometallurgical processes. These products are important not only as they may present environmentally undesirable material if dumped but also they may contain metal values that are higher than those contained by the original ores. Quite often precious metals such as silver, gallium, indium and gold may be concentrated in these residues and this increases the attractiveness of further treatment. Many of these residues may be recycled in smelters and periodically tapped to avoid poisoning of the smelter by such elements as arsenic and sulphur. However, this material must ultimately be treated if it is to be safely dumped. Current research in this field is involved with the characterization of these fine grained materials to gain a deeper understanding of their constituents to aid in choosing the best form of treatment.

On the face of it, this may appear to be a simple task but, in the case of

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the non-ferrous ores, the products formed by metallurgical processes tend to be quite complex. This is due to the complex nature of the ores themselves and also to the number of chemical reactions that may take place during the refining processes. Although metal concentrations may be determined by atomic absorption spectrometry and XRF, information on the kind of compounds formed is essential in the treatment of these residues. X-ray diffraction is only of limited use as many products are poorly crystalline, very fine grained and give complex patterns that are difficult to deconvolute. Consequently, analytical electron microscopy is a useful tool in providing information on morphology, chemistry and particle-to-particle associations in these materials.

The use of electron microscopy in this area can be best explained by using some examples of the materials under study, but sample preparation is worth mentioning before continuing. The majority of these residues are composed of particles of less than $50\mu m$ and may reach sizes of less than $0.5\mu m$. Adequate dispersion of samples is very important as (especially in the case of pyrometallurgical residues) it is necessary to know if particles of different compositions are intrinsically bonded to one another or are simply in close juxtaposition due to the sample preparation technique (Figure 1). This effectively rules out air dispersion on SEM stubs, as particles of this size are susceptible to electrostatic attraction and form tight agglomerates which can present difficulties in analysis. Consequently, dispersion in a liquid has proved to be more suitable, and filtration through polycarbonate filters provides a smooth surface for subsequent SEM analysis. The same filter can be used for preparing TEM or STEM samples by the Jaffe Wick method of coating the filter surface with evaporated carbon, removing a small portion of the filter and laying it on the top of a 200 mesh electron microscope grid in the Jaffe Wick apparatus. The filter is dissolved by chloroform, leaving the particles embedded on the carbon film on top of the grid, ready for viewing in transmission mode. Various liquids were tested by the authors and propanol proves to be the best medium for

dispersion of these residues. An initial dispersion of approximately 1.0×10^{-4} g/cm³ to provide a solids concentration on the filter of 3.0×10^{-5} g/cm² is enough to give satisfactory dispersion.

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Analysis of the untreated dust from copper smelters presents a number of problems due to the number of phases present and fusing of phases in a high temperature-corrosive atmosphere. This problem can be partially overcome by acid leaching in $2.5M H_2SO_4$. Such leaching effectively removes copper and zinc oxides while leaving iron oxides, lead sulfate and silicates in the residue. Further separation can be achieved by high grade magnetic separation which separates the iron-fraction from lead and silicate phases. On the face of it, no further analysis should be necessary as the individual fractions can be treated to render the metal values contained within them. However, laboratory and plant testing shows that only 50 % Zn and 30 % Cu is removed by the leaching stage and 20 % Pb may report to the magnetic product after leaching while 5% Fe and 14 % Zn report to the non-magnetics.

X-ray diffraction gives some pointers as to why such imperfect separation may occur. For instance, much of the Zn and Cu are present as ferrites. These are spinel type compounds with a structure similar to that of magnetite. They tend to be resistant to attack and may be more or less susceptible to magnetic separation, depending upon the Cu:Zn ratios present in their structure. Figure 2 shows a twinned magnetite crystal from the magnetic fraction. This is worthy of note as the crystal is only 5 μ m in diameter. Most magnetite is well crystallized and EDS analysis of the crystal shows that Fe is the only major EDS peak.

Figure 3 shows a backscatter image of a particle of Cu-Zn ferrite in the magnetic phase. It can be seen that the ferrite does not display the same degree of crystallinity but is spherical, indicating rapid cooling from the molten state. EDS analysis indicates a significant proportion of lead associated with this particle. Further observation of the backscatter image shows a network of more electron dense material on the surface of the ferrite. This can be explained by deposition of more volatile lead or $PbSO_4$ on the surface of the ferrite as it cooled. Due to the fact that this material will be tightly bonded to the ferrite surface, it is carried over into the magnetic fraction with the ferrite.

The opposite effect may also take place if a ferrite particle is heavily coated with lead salts; this particle will report to the non-magnetic fraction. Other particles present in the non-magnetic contain copper but not iron (Figure 4). Although EDS analysis cannot detect the presence of oxygen it is likely that the copper and sinc oxides would be removed by the acid leaching. Consequently, these particles represent intermetallics that are fugitive from the copper melt.

It can be seen that treatment of these precipitators dusts can present complex problems. Only 50 % Zn and Cu is easily removed by acid leaching with H_2SO_4 —a material readily available on site. Furthermore 20 % Pb may be lost to the magnetic fraction during high grade magnetic separation due to bonding with ferrites. This is especially important as some precious and semi-precious metals such as silver may be associated with the lead. Further research on precipitator dusts and residues from electrolytic plants indicates the value of electron microscopy in determining process metallurgy for retreatment of these materials. Figs. 5 and 6 represent secondary electron and backscatter images of ponded zinc ferrite material from an electrolytic zinc plant. EDS analysis indicate a minor silver-bearing lead fraction, and it can be seen in the backscatter image that this lead is, in fact, discrete and could be retrieved by physical separation. EDS analysis to give Zn:Fe ratios may act as an indicator to the magnetic properties of ferrites formed under different temperature conditions, hence aiding in defining conditions for suitable separation.

In conclusion, it can be seen that electron microscopy is a valuable tool in the characterization of fine grained metallurgical residues. Sometimes this is the only technique that can provide the information necessary for the processing of these wastes. Further applications of electron beam technology in the field of process

mineralogy include image analysis for phase sizing, distribution analysis and liberation studies; Auger spectroscopy in studying surface properties of particles (often a very critical parameter in separating minerals), and the use of EELS and windowless EDS detectors for the determination of non-crystalline oxides, sulphates and intermetallics. It is certain that the treatment of more complex materials and ores necessitate further use of such instruments in the future to aid in interpreting processing strategy.

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Figure 1 Backscatter image of poorly dispersed dust showing particle overlap.

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Figure 2 Twinned magnetite crystal (secondary electron image)



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Figure 3 Cu-Zn ferrite with partial PbSO₄ coating (backscatter image).



Figure 4 Cu-Zn intermetallic (secondary electron image).



Figure 5 Ponded zinc ferrite (secondary electron image).



Figure 6 Ponded zinc ferrite (backscatter image).

Connecting Text for Manuscript II: Characterization and Separation of a Copper Smelter Dust residue

Some of the results of the characterization of the Kidd Creek copper smelter dust were included in Manuscript I. Manuscript II presents more fully the results of the characterization of the copper smelter dust.

Manuscript II also explores the potential application of hot sulfuric acid leaching and magnetic separation of the components of the acid leach residue.

MANUSCRIPT II

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Characterization and Separation of A Copper Smelter Dust Residue

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CHARACTERIZATION AND SEPARATION OF A COPPER SMELTER DUST RESIDUE

Lastra, R., Rowlands, N., Rao, S.R., Finch J.A.

ABSTRACT

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> Kidd Creek copper smelter Cottrell dust was characterized. It was 88 % finer than 8μ m and contained 21.3 %Zn, 26.2 %Pb, 10.6 %Cu, 1.8 %As, 1.4 %Sn, 0.6 %Cd and minor amounts of Bi, Co and In. The phases positively identified were: PbSO₄, ZnO, ZnOFe₂O₃, ZnS, Cu₂O, Cu₂OFe₂O₃, and Cu₃As. Processing in a 1.5M H₂SO₄ leach followed by magnetic separation of the leach residues achieved a 50-60 %Zn and 60 %Cd recovery to the leach liquor; over 40 %Fe to the magnetic fraction and over 80 %Pb, As, Sn to the non-magnetics.

INTRODUCTION

Processing of smelter and refinery solid wastes for recycle, production of saleable products, or simply safe disposal, is becoming increasingly important due to economic and environmental pressures.

As an aid in determining the process route it is necessary to know not only elemental but mineralogical (or phase) composition. Mineralogical data is difficult to obtain on these complex materials due to the formation of multi-element complexes with varying degrees of crystallinity. Results of examination of the mineralogy and some separation options on a copper smelter dust from Kidd Creek Mines are presented in this paper. The Kidd Creek copper smelter is based on the Mitsubishi Process. This consists, briefly, of three furnaces, interconnected by gravity launders. One of the furnaces is for smelting, one for converting and another for slag cleaning. Typical analyses of the most important inputs and outputs to the process are given in Table 1. The feed rate is around 55 MTPH.

Table 1. Main Inputs and Outputs to Mitsubishi Process at Kidd Creek.

[%Cu	%Fe	%s	% Рь	%Zn	Nm ³	% SO2	%O ₂	$\% N_2$
Copper Conc.	26.5	28	32	0.5	4		-	_	
Matte	67.5	7.5	21.5	0.4	1	—	-		
Discharge Slag	0.8	40	0.6	0.2	4		-	_	—
Recycle Slag	20	35	1.0	0.8	3	_	-		
S Boiler Gas	-	-	-	-	_	63E	24	1	73
C Boiler Gas	-	-	-	-	-	431	17	3.1	74

Besides the main products, dusts are also formed during the smelting process which are trapped in Cottrell precipitators. Approximately 80 tonnes are produced daily and these dusts are rich in copper, zinc and trace elements such as silver, cadmium and indium. In addition, less desirable elements such as iron, lead and arsenic are also present. The Cottrell dusts are presently treated with sulphuric acid in the zinc plant for removal of zinc and copper. Only partial recovery is attained. This study deals with the characterization of the material with view to developing recovery process. In order to predict suitable techniques for phase separation the material was first characterized using a combination of analytical methods. The application of electron microscopy and X-ray diffraction has already been successfully applied to understand the nature of phase relationships in much simpler iron arc-furnace dusts [1].

MATERIAL DESCRIPTION

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Particle Size and Chemical Composition

The copper smelter dust is collected in Cottrell precipitators, slurried and transported to the zinc plant [2]. The material tested was that received at the zinc plant i.e. after water soluble components had been removed. (In the text the term "Cottrell dust" will often be used, but this is to be understood as the residue of this water leach.)

The sample contained about 45 % moisture with a solids specific gravity of 4.506, determined by pycnometer. Cyclosizing showed about 88 % passes 8μ m and the sample contained (from atomic absorption spectroscopy) 6.0%Fe, 21.3%Zn, 26.2%Pb, 10.6%Cu, 1.8%As, 1.4%Sn, 0.6%Cd. There was no strong variation in composition with size.

Mineralogical Analysis

The Cottrell dust was studied by X-Ray diffractometry (XRD). The XRD pattern showed peaks of low intensity suggesting phases of poor crystallinity. The XRD pattern showed many peaks which complicated the task of phase identification. To aid the identification, likely compounds were predicted from thermodynamics. The chemical analyses showed that the dust contained mainly Zn, Pb, Cu, Fe and As and it was known that the dust was coming from a process where the major gases are SO₂ (17-24%); O₂(1-3%) and N₂(\approx 74%) at a temperature of 1473 K [4]. Using the EQUILIB program of F*A*C*T (Facility for Chemical Thermodynamics [3]) a list of possible phases was drawn up. The compounds in this list were then used to help identify the XRD peaks. Later further evidence was found to support the existence of some phases which were concentrated after leaching or magnetic separation. A summary of chemical and phase composition of the dust is given in Table 2. The phases are classified as positively or tentatively identified.

Scanning electron microscopy (STEM-JEOL 100CX) with energy dispersive analysis (EDS) was performed on individual particles for morphological and chemical characterisation of individual phases. Two distinct morphologies were evident "spherical" (Figure 1) and "irregular" (or "slag-type") (e.g. Figure 2). Both particles appear to be formed by accretion of smaller particles ($\approx 0.1 \mu m$). The spherical particles were characterized by low iron content, but could be either sinc-rich (e.g. Figure 1), copper-rich or lead-rich. The irregular shaped particles were richer in iron (e.g. Figure 2) but also contained appreciable Zn, Cu and Pb. The SEM and X-ray fluorescence analysis also revealed the elements As, Sn, Cd, Bi, Co, and In.

Table 2. Chemical composition and phases present in the Cottrell dust.

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		z	PHASE IDENTIFIED / 1 POSITIVELY	IDENTIFICATION NETHOD TENTATIVELY
	РЪ	26 . 2	Pb804/ 1,2,5,7,9	Cu/Zn/Pb metalice 14 PbO-PbSOg /1
	Za	21.3	ZaO / 1,2,4,15 ZaOFe20g/ 1,2,5,7,8,9 ZaS / 3,4,7,8	Cu/Zn/Pb metalics /14
	Cu	10-6	Cu20 / 1,16 Cu207e203/ 1,12,8	Cu-S compounds / 6,8 Cug res 4 /1
	7e	6.0	ZnOFe ₂ 03/ 1,2,5,7,9,9 Cu ₂ 0Fe ₂ 03/ 1,12,8	Feg04/ 1,2
	As	1.8	Cu3As /1, 17	Asg03/ 1.2 Asg ¹ 4/ 18
	Cđ	0.6		Cd-compounds / 10,11,13
	Sn	1.4		Sa-compounds / 10,11,13
	B1			Bi-compounds / 10,11,13
	Co			Co-compounds / 10,11,13
	In			In-compounds / 10
1. 2. 3. 4. 5. 6. 7. 8. 9. 10. 11. 12. 13. 14. 15. 16. 17. 18.	Thermodynamic X-ray diffrac SEM of origin Indirect; fro IRD of 1.5 to SEM OF 0.5M H XED for produ XED for produ XEF of HgS04 Indirect; fro XEF for produ SEM for non- MED of 0.5 to XED of non- MED of non- MED of non-	predict: ition of (al Cottro x-ray i) 2.5MH25(2504 lead cts of Fi cts of Fi al Cottro leach ref the XBI cts of Fi agnetic l 2504 lead 1.5M H20 gnetic pi -magnetic se search	ion original Cottrell dust all dust fluorescence (XRF) of H ₂ SO ₄ lead Og leach residues. ch residue rentz magnetic separation igh gradient augnetic separation all dust sidues D of H ₂ GO ₄ leach residues rentz magnetic separation Frantz product from a 2.5M H ₂ SO ₄ ch residue SO ₄ leach residue roduct of 1.87T HCMS. Pha h program (Philips APD1700)	ch residues n (HGMS) g leach residue nee listed between the posssible phases by an
*.	Za804, Zn0-Z dissolved of	n SO4, and slurrying	d CuSOg are also predicted by the glust with water.	mermodynamic analysis, but are

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SULPHURIC ACID LEACHING

Procedure

Leaching tests were conducted by mixing the as received Cottrell dust with sulphuric acid of concentration in the range 0.5 to 2.5 M and heating to boiling. Pulp density was fixed at 50% solids by weight. The optimum leach time was determined by recording the percent weight loss of solid with time. No further weight loss was observed after 20 minutes at any acid strength. Consequently 20 minutes was chosen for all leaching tests. After leaching the slurry was cooled; the supernatant was decanted and the residual solids washed 6-8 times with distilled water and dried. The solids were assayed and examined mineralogically.

Results

Figure 3 shows the percent metal and phase remaining in the residue with increasing acid concentration. Phases were identified by XRD; peak heights were used as a semi-quantitative measure of phase concentration.

Zinc dissolution appears to be a combination of rapid ZnO leaching and relatively slow ZnOFe₂O₃ leaching. Copper removal is related to Cu₂O leaching but clearly Cu₂O does not account for all the copper present in the dust. This provides indirect evidence of refractory phases, such as copper ferrite. The latter is predicted thermodynamically but it is \vdots -possible to differentiate from zinc ferrite by XRD. Figure 4 shows a Cu-Zn sulphide in the residue of the 0.5M acid leach; copper and zinc sulphides are relatively insoluble in H₂SO₄ [6] and they have been previously observed in the Cottrell dust [5]. Particles containing metallic copper have also been observed [5] and considering that the genesis of such particles was in atmospheres containing sinc, then the presence of Cu-Zn metallics is also probable. It is known that copper and zinc can give rise to some alloys that resist H_2SO_4 attack [7]. A non-magnetic fraction of the 2.5M leach residue was isolated on the Frantz isodynamic separator to try to concentrate this phase. Figure 5 shows a particle with high Cu and Zn, low Pb, and Fe and no S. This is taken as evidence of a Cu-Zn metallic in the Cottrell dust.

From a process standpoint, the results at 1.5M are probably optimum, about 50 %Zn, 30 %Cu, and 60 %Cd are recovered in the leach liquor with less than 10 %Fe and Pb.

MAGNETIC SEPARATION

Separation on the Frantz isodynamic separator

Figure 6 gives the magnetic profile [8] for Cyclosizer cone 3 ($\approx 15\mu$ m) of asreceived material and residue from the 1.5M acid leach. In both cases a highly magnetic fraction (I<100 mA) occurs. This fraction has a I₅₀ \approx 70 mA indicating a susceptibility about 7-8×10⁻² SI units (at 0.08 tesla). This is greater than that of zinc ferrite suggesting the presence of copper ferrite and iron ferrite (magnetite).

Each current (i.e. susceptibility) increment was assayed for Zn, Fe and Pb and a separability curve was constructed. Figure 7 shows the result for the residue of the 1.5M leach. Iron is recovered into the mags, and lead into the non-mags; zinc essentially splits evenly. Since there is no strong variation in chemical composition with size, this separability curve should approximate that of the whole sample.

SEM analysis of the most magnetic fraction (50 mA) showed Fe-rich particles with the slag-type morphology as shown in Figure 8. A standardless semi-quantitative analysis for the EDS spectra of several particles gave an average wt %Zn:wt %Fe ratio of 0.5. This is close to the theoretical value for zinc ferrites. Figure 8, also shows the X-ray map for Cu (X-ray production depth for copper is $\approx 6 \ \mu m$ [9]). The copper is present as ferrite and the lead and sulphur are present as PbSO₄. The latter is a separate phase which is agglomerated to the ferrite, as illustrated by the electron backscatter image in Figure 9. This particle heterogeneity will limit physical separability.

High Gradient Magnetic Separation (HGMS)

Procedure

The matrix was built of 28 expanded metal sheets, with diamond-shaped holes and wires of diamond cross-section with a hydraulic diameter of 0.5 mm. The spacers were held in vertical array with the sheets separated by 1.5 mm aluminum spacers. (A vertical array reduces non-magnetic entrapment and allows passage of the small fraction of larger particles [10]). The matrix was 6 cm long by 4×4.5 cm square with a mass of 46.6 g and was held in a Plexiglas container. The HGMS was an Eriez Magnetic model EL5-4.

Both as-received and samples after leaching at 1.5M acid were processed. Thirty-grams samples were dispersed in 300 ml 0.1% Calgon solution by 30 minutes ultrasonic agitation. A single pass at fields up to 1.8T and superficial liquid velocities of 9.7 cm/s was used.

Results

Figure 10 shows the separation achieved on leached material. Increasing field has little effect. In agreement with Figure 7, iron is preferentially recovered to the mags, lead to the non-mags while zinc splits between the two fractions.

Figure 11 shows the separation achieved by a combination of leach and HGMS. The most important separations achieved are: 50-60% Zn and Cd to leach liquor; over 40% Fe to mags; over 80% Pb, As, Sn to non-mags.

DISCUSSION

Mineralogy

By a combination of techniques, including thermodynamic predictions, some nine phases were positively identified. The major elements are Fe, Zn, Cu, and Pb. Assuming Fe, Zn, and Cu occur as oxides and Pb as the sulphate, as indicated by the mineralogical evidence, then over 95% of the mass is accounted for these elements. Several more trace elements were identified by atomic absorption and/or X-ray fluorescence but their phase relationships were not positively identified. (Table 2).

Two distinct morphologies were found. The spherical particles were Fe-poor, the slag-type particles Fe-rich. This may correspond to the higher fusion temperatures of iron oxides (Fe₃O₄ fusion temp. is 1870 K [11]) at the prevailing gas temperatures, the Fe-poor particles may have fused and consequently become rounded. Three magnetic oxides were identified, $ZnOFe_2O_3$, $Cu_2OFe_2O_3$ and Fe_3O_4 .

Electron Microscopy observation of some ferrites showed from iron-X-ray maps more concentration of iron towards the centre of the particle. Based on this a speculative mechanism of ferrite formation may be proposed. Solid iron oxides act as reaction centres where Zn (vapour) and Cu {liquid} oxidize and are fixed, according to:

$$\langle Fe_2O_3 \rangle + (Zn) + 0.5(O_2) = \langle ZnOFe_2O_3 \rangle \qquad \Delta G^{\circ}_{1473} = -169.87 \text{kJ}$$

$$\langle Fe_2O_3 \rangle + 2\{Cu\} + 0.5(O_2) = \langle Cu_2OFe_2O_3 \rangle \qquad \Delta G^{\circ}_{1473} = -69.04 \text{kJ}$$

This agrees with the proposal of Yargin et al. [12]. The higher (negative)

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free energy favours zinc ferrite formation which agrees with the predominance of Zn-ferrite over Cu-ferrite.

Other copper and zinc phases were unreacted sulphides, presumably fugitive particles from the reactor and a trace amount of Cu-Zn metallics, presumably from splashing of the melt.

A common feature to all particles was their highly agglomerated and chemically heterogeneous state. This reflects the high gas temperatures leading to fusion. Figure 9 shows a classic limitation to physical separation, some lead sulphate is clearly bound to the magnetic phases. Agglomeration poses little restriction to leaching as the agglomerates are fine and probably porous. It was felt that leaching may help release phases for subsequent magnetic separation. Figure 6 supports this view, but comparative separation tests on leached and un-leached samples showed no significant gain.

Metallurgy

The present results show that a $1.5M H_2SO_4$ leach of a copper smelter dust can recover to the liquor nearly 30%Cu, 50%Zn and 60%Cd with less than 10%Fe and 5%Pb recovery. (This is in addition to the Cu, Zn solubilised on slurrying the original dust in water for transport to the zinc plant). This leach liquor can be introduced into the zinc plant circuit for recovery of these metals.

Recovery of the magnetic fraction is facilitated by this fraction's high susceptibility. However, particle heterogeneity limits the separation potential. The magnetic product contains the bulk of the refractory oxides suggesting that this product may best be disposed off without further treatment (however the recycling or retreatment to more intensive processes should be evaluated). Unfortunately the magnetics do not retain the As and Cd which would enhance the value of magnetic separation as a means of concentrating deleterious materials for disposal. The non-magnetic product can be considered as a lead concentrate or a bulk Pb/Zn concentrate. The silver content is not known but clearly this would be important given the current (and projected) market for lead.

The potential of magnetic separation on other residues from the sinc plant (namely the jarosite and hot-acid-leach residues) is being pursued.

ACKNOWLEDGEMENTS

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Figure 1 Example of spherical morphology. The energy dispersive (EDS) ratios relative to zinc are: Zn 1.0; Fe 0.04; Cu 0.34; Pb 0.07; As 0.07; S 0.01.



Figure 2 Example of irregular ("slag-type") morphology. The EDS ratios relative to zinc are: Zn 1.0; Fe 0.37; Cu 0.65; Pb 0.44; As 0.43; S 0.98.


Figure 3 Dissolution as a function of acid concentration (Note: Cd dissolution was 60%, As and Sn dissolution 0%).

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Figure 4 Fugitive Cu-Zn sulphide particle found in the residue of the 0.5M acid leach. EDS ratios relative to zinc are: Zn 1.0; Fe 0.01; Cu 0.90; Pb ≈0; S 0.62.



Figure 5 Particle in the 75 mA non-magnetic Frantz fraction from the 2.5M leach residue. EDS ratios relative to zinc are: Zn 1.0; Fe 0.08; Cu 0.49; Pb 0.06; S ≈0.



Figure 6 Magnetic profile of Cottrell dust residues (Cyclosizer cone 3 fraction)

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Figure 7 Separability curve (recovery vs. yield) for 1.5M leached samples. Head assay was 10.8% Fe, 14.7%Zn and 29.9%Pb.



Figure 8 Typical particle in the 50 mA Frantz magnetic fraction. The slag-type morphology is evident. (Bright dots show the Cu-X-ray map.) The EDS ratios relative to zinc are: Zn 1.0; Fe 2.73; Cu 0.60; Pb 0.98; S 0.95.



Figure 9 Electron backscatter image. Shows the close association of several phases. Brighter areas are PbSO₄.



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Figure 10 HGMS separation on 1.5M leached samples as a function of field strength (flow rate was 9.7 cm/s).

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Connecting Text for Manuscripts III and IV: Characterization and Separation of Residues from the Kidd Creek Zinc Plant

Independent studies [92] on the Kidd Creek Copper smelter dust have shown the feasibility of recycling the dust to the zinc plant of the same company. Presently Kidd Creek follows that practice. At that facility, the copper smelter dust undergoes H_2SO_4 leaching. This leach treatment coincides in general with the proposed flowsheet in Manuscript II (see Figure 11 in Manuscript II). However no magnetic separation of the leach residues is performed in the Kidd Creek zinc plant.

In the Kidd Creek metallurgical complex the copper smelter dust is slurried and transported to the zinc plant. The Cottrell dust is an additional part of the feed to the zinc-leaching circuit; the main part being roasted zinc concentrate (primarily zinc oxide calcine), also unroasted zinc concentrate is feed to a pressure leach process. In the zinc plant two other residues are produced: the jarosite residue and the hot-acid leach (HAL) residue (Figure 1 of Manuscript IV gives an overall flowsheet of the zinc-leaching circuit). Manuscript II showed that zinc ferrite is one of the phases present in the Cottrell dust. Zinc ferrite is also one of the constituents of the zinc oxide calcine. The flow-sheet of Figure 1 in Manuscript IV shows that any zinc ferrite that cannot be dissolved in the H_2SO_4 leach of the copper Cottrell dust will report to the jarosite residue. However, calcine is also added to other parts of the circuit, for pH control, consequently the jarosite residue will also receive sinc ferrites from that source. The HAL residue will also have zinc ferrites that could not be dissolved and that come into the circuit with the calcine feed to the neutral leach and to the low acid leach. Zinc ferrites in these residues represent

a loss of sinc, consequently if further recovery of sinc is sought then these residues should be considered for recycling or separate treatment. A detailed knowledge of the minerals or phases present would help in determining possible routes for their processing; also the potential of the application of magnetic separation for these residues was considered.

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Manuscripts III and IV both deal with the characterisation of the jarosite and the HAL residues; however the emphasis in Manuscript III is on the characterisation by EM methods, while Manuscript IV includes the evaluation of magnetic separation on this residues.

MANUSCRIPT III

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Characterization of Residues From A Zinc Plant

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CHARACTERIZATION OF RESIDUES FROM A ZINC PLANT

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INTRODUCTION

Metallurgical wastes of various compositions are generated at various stages of operation in a zinc extraction plant. These residues still contain significant quantities of zinc, lead, and copper. The recovery of these valuables could be of economic significance. As an aid in determining possible process routes for their treatment, a detailed knowledge of the mineral or phases present is required.

JAROSITE

Separation of iron from zinc in zinc leaching circuits is usually done by jarosite precipitation in which iron and other impurities are rejected. Composition of jarosite is expressed by MFe₃(SO₄)₂(OH)₆ where $M = K^+$; Na⁺; NH⁺₄; Ag⁺; $\frac{1}{2}Pb^{+2}$; H₃O⁺; etc. [2]. Also it appears [3] that divalent ions such as Cu⁺² and Zn⁺² may partially replace Fe⁺³ in the jarosite lattice, producing small but unwanted losses.

The jarosite residue as received was a reddish-brown bulk material. Chemical analysis was determined by atomic absorption (AA) and yielded 7.24%Zn, 38.76%Fe, and 1.61%Pb. Size analysis by Cyclosizer showed that nearly 90% of the material is <10 μ m. X-ray diffraction (XRD) patterns of the Cyclosizer products were obtained and the two main crystalline phases were identified: sodium jarosite, NaFe₃(SO₄)₂(OH)₆; and zinc ferrite, ZnFe₂O₄. It was found that the fraction \geq 15.2 μ m carried higher proportions of ZnFe₂O₄. However, AA analysis showed that the \geq 8.2 μ m fraction still carried 67 % of the zinc contained in the sample.

Knowing that sinc ferrite shows a paramagnetic behaviour it was then decided to determine the magnetic profile of the fraction $\geq 15.2 \ \mu m$ by use of a Frantz isodynamic separator. The division of the jarosite residue into a series of products obtained by their different behaviour under magnetic field provided a powerful tool for further characterization of the sample, since these Frantz products were less complex than the original residue. Table 1 provides the results of the magnetic separation, together with the XRD intensities in counts per second, of the strongest peak of the two main components. From Table 1 it is possible to see that the zinc ferrite concentration in the magnetics increases as the current increases, up to 250 mA, where the ratio $I_{100}ZnFe_2O_4:I_{100}Na$ -jarosite is 40:1. After this point, the magnetics show increasing amounts of jarosite up to 500 mA, where the product is almost only Na-jarosite; their corresponding magnetic susceptibilities are 7.61×10⁻³ and 1.03×10^{-3} SI units, respectively. The non-magnetic of 600 mA contained both zinc ferrite and Na-jarosite as minor constituents.

SEM of the 250 mA Magnetic Product

Figure 1 illustrates the type of particles most frequently encountered. The average EDS Zn/Fe ratio in this type of particles was around 0.6, which suggest that these particles are indeed zinc ferrite. Copper is present mainly at low concentrations; the EDS Cu/Fe ratio most often encountered was around 0.07. Previous

studies with zinc ferrites in the copper smelter dusts [1] have shown that the amount of copper in the zinc ferrites plays an important role in their magnetic susceptibilities and may increase it to 7.5×10^{-2} SI units when the EDS Cu/Fe ratio is around 0.9.

SEM of the 500 mA Magnetic Product

Figure 2 shows the typical particles found in this product. Their morphology and EDS peak counts are characteristic of the jarosites. It was possible to find in them variable minor amounts of Cu, Zn, As, and Pb. X-ray mapping for these elements showed an even and intimate distribution in all particles. This result is in agreement with Dutrizac's findings [3] and suggest that these elements are incorporated in the jarosite lattice.

SEM of the Non-magnetic Product of 600 mA.

The most abundant particles in this product gave large EDS Si counts, which indicated the presence of SiO₂.

A large variety of other particles were found in this product. Figure 3 shows a particle with EDS counts indicating zinc sulphide. Figure 4 presents a particle with large Si and Sn contents. The presence of Sn is not surprising since the Kidd Creek ore body contains tin-bearing minerals [4]. Figure 5 shows the remains of a once-locked particle: the Zn-S-O compound (either oxide, sulfate, or sulfite) was readily dissolved but the base metal silicate remains insoluble. Finally, Figure 6 shows a particle with morphology and composition typical of the alkali-feldspar family: (KNa)AlSi3O₈ with minor amounts of Zn, Fe, and Cu. The alkali-feldspar family occurs in the county rock of the Kidd Creek ore body [4].

Table	1.	X-ray	diffracti	on inte	ensities	of two	strongest	peaks	for	the
tvi	юп	nost ab	undant	phases	in Fra	nts pro	ducts.			

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Frantz Product	ZnFe ₂ O ₄ I ₁₀₀ [cps]	Na-jarosite I ₁₀₀ [cps]	$\frac{I_{100}ZnFe_2O_4}{I_{100}Na - jarosite}$
Magnetic of 50mA	981	90	11.0
Mag. of 200mA	927	80	11.6
Mag. of 250mA	1133	28	40.0
Mag. of 300mA	605	1 36	4.0
Mag. of 400mA	737	172	4.0
Mag. of 450mA	77	448	0.2
Mag. of 500mA	-	560	-
Mag. of 550mA	-	452	-
Mag. of 600mA	-	264	-
Final non-magnetic	84	84	•

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SILVER-LEAD RESIDUE (HOT-ACID-LEACH RESIDUE)

This is the solid residue after three stages of sulfuric acid leaching, with some of those leaching stages being performed at $\approx 90^{\circ}$ C. The residue was studied in a way similar to that used for the jarosite residue. Its determined AA analysis gave 9.80%Zn, 11.72%Fe, 7.94%Pb, and 0.60%Cu. Size analysis by Cyclosizer gave 85% <8.2 μ m.

The HAL residue was separated into products according to their magnetic behaviour using the Frantz apparatus. XRD of these Frantz products showed zinc ferrite to be the major mineral phase in the magnetics separated at 50 to 500 mA. However, the product richest in zinc ferrite was that of 300 mA. The determined magnetic susceptibility for zinc ferrite in the HAL residue was $\approx 5 \times 10^{-3}$ SI units.

SEM of the 50 mA Magnetic Product

This is the first magnetic product of the Frantz series. Two main morphologies were found. Figure 7 shows the most abundant type of particles; their EDS peak counts indicate zinc ferrite. The second most abundant type of particles is seen in Figure 8; they show large Fe counts but also large Pb and S counts together with some Zn and Cu counts. An automated search-and-match program of the XRD pattern of this magnetic product identified the presence of $ZnFe_2O_4$ and $PbCS_3$.

SEM of the 300 mA Magnetic Product.

Figure 9 shows the most abundant type of particles in this product. The large EDS counts of Fe and Zn indicate a zinc ferrite particle. The wt% ratio for Zn/Fe for these particles is ≈ 0.47 (determined by ZAF-corrected EDS analysis), which suggest that some zinc has been leached out. The corresponding ratio for Cu/Fe is only ≈ 0.03 , which agrees with the low magnetic susceptibility of the zinc ferrite in the HAL residue. The particle in Figure 9 also shows small amounts of Pb-S compounds.

In this product it was possible to find particles of hematite (see Figure 10) and of MnO_2 . The presence of MnO_2 is explained as an excess of the added in the first leaching steps to reduce the undesired concentration of ferrous iron [5].

SEM of the 600 mA Non-magnetic Product.

Most of the particles in this product suggest the presence of SiO_2 ; Figure 11 shows an example. Also it was possible to find particles with large Si counts and appreciable Cu, Fe, and Zn counts. Together with strongly angular features, that suggests the existence of base-metal silicates.

An automated search-and-match program was used further to identify the XRD patterns of various magnetic and non-magnetic products of jarosite and HAL residues. The success of the search program depends heavily on a provided list of known elements. Therefore, the results obtained by SEM-EDS were used to give a partial list of elements present in the products. The results of this automated search-and-match program confirmed the existence of the suggested phases by SEM-EDS and also added the presence of few other phases.

CONCLUSIONS

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1. The evidence collected by SEM and XRD showed that jarosite residue is made up of the major abundant phase (% >10) of Na-jarosite, with some small quantities of Zn, Cu, and As incorporated in the crystal lattice; the medium abundant phases (10 > % > 1) are zinc ferrite associated with copper ferrite in small variable amounts and SiO₂; and other phases encountered in small proportions (% <1), which in order of abundance are feldspars, ZnS, FeS, Cu₂FeSnS₄, Cu(Fe,Sn)₂S_{3.9} and Cu-Zn-Fe-Sn silicates.

2. The collected evidence showed that the HAL residue were found to be, as the most abundant phases (% >10), $ZnFe_2O_4$, Fe_2O_3 , and SiO_2 ; as medium abundant phases (10 > % >1), SnO_2 , $PbCS_3$, $PbFe_6(SO_4)_4(OH)_{12}$, ZnS, and CuS_2Sb ; and as minor abundant phases (% <1), MnO_2 , FeS, Cu_3FeS_4 , Fe_9S_8 , S, and Cu_2FeSnS_4 .



H.G. 1.--IDS peak ratios (LDSPR) to Fe are: Fe 1.0, Zn 0.62; Cu 0.07.
H.G. 2.--IDSPR to Ie: Ie 1.0, S 0.11, Cu 0.09, Zn 0.02, Na 0.00109.
H.G. 3.--IDSPR to Zn are: Zn 1.0, Ie 0.03, S 0.1.
H.G. 4.--IDSPR to Sn are: Sn 1.0, Si 0.03, Cu 0.01, Zn 0.01, Fe 0.01, S 0.0004.
H.G. 5.--IDSPR to Si are: Si 1.0, Zn 0.77, Fe 0.32, Cu 0.16, S 0.14, Pb 0.14, A1 0.07.
H.G. 6.--IDSPR to Si are: Si 1.0, Al 0.76, K 0.37, Zn 0.31, Fs 0.16, Cu 0.05.



FIG. 7.--EDSPR to Fe are: Fe 1.0, S + Pb 0.15, Zn 0.14, Cu 0.01 FIG. 8.--EDSPR to Fe are: Fe 1.0, S + Pb 1.04, Zn 0.12, Cu 0.03. FIG. 9.--EDSPR to Fe: Fe 1.0, Zn 0.19, S + Pb 0.09, Cu 0.01. FIG. 10.--EDSPR to Fe: Fe 1.0, Zn 0.02, Cu 0.01. FIG. 11.--EDSPR to Si: Si 1.0, Fe 0.11, Cu 0.14, Zn 0.08, Mn 0.05.

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MANUSCRIPT IV

Characterization and Separation of Metallurgical Residues from the Kidd Creek

Zinc Processing Plant

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CHARACTERIZATION AND SEPARATION OF METALLURGICAL RESIDUES FROM KIDD CREEK ZINC PROCESSING PLANT

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ABSTRACT

Two of the major residues that are generated in the extraction of zinc are jarosite and hot-acid-leach residues. Some still contain significant metal values. Samples of the two residues from the metallurgical plant of Kidd Creek Mines, Ltd., Ontario, Canada, were examined. Particle-size analysis showed that both residues were fine, 80 wt % being -12 μ m. The major phases identified in the jarosite residue were sodium jarosite and zinc ferrite and in the HAL residue zinc ferrite, hematite, silica and lead jarosite. Some evidence was found for lead sulphate/oxy-sulphate in the HAL residue.

Magnetic analysis gave a zinc ferrite susceptibility of $4-8 \times 10^{-3}$ in both residues; sodium (and lead) jarosite were also magnetic, their susceptibility being 1.0×10^{-3} . High gradient magnetic separation recovered some 20-40% Zn from the jarosite residue at zinc grades of 15-10%. From the HAL residue 20-30% Zn was recovered at sinc grades of 22-18%. The limits to separation are discussed.

INTRODUCTION

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Metallurgical wastes of different compositions are generated at various stages in a sinc extraction plant. These residues still contain significant quantities of sinc, lead and copper and the recovery of some of these values could be of economic significance.

A description of the nature and processing of Cottrell dust residue from the metallurgical plant of Kidd Creek Mines, Ltd., Timmins, Ontario, Canada, has been given elsewhere [1]. In the present study two more metallurgical residues from the plan were examined —the jarosite residue and the hot acid leach residue (HAL), or lead-silver residue, (Figure 1) [2]. A significant part of the zinc in the residue is present as zinc ferrite —which is appreciably magnetic, suggesting the possibility of recovering zinc magnetically. To develop a suitable magnetic processing method it is necessary to identify the different phases and to determine their magnetic characteristics. This was achieved, respectively, by analytical techniques (X-ray diffraction (XRD) and scanning electron microscopy (SEM) with energy dispersive spectrometry (EDS) for semi-quantitative elemental analysis) and by the use of a Frantz isodynamic separator. On the basis of the findings, high gradient magnetic separation (HGMS) was studied for the recovery of zinc ferrite.

THE JAROSITE RESIDUE

Description

The separation of iron from zinc in zinc processing circuits can be achieved by precipitating iron as jarosite $MFe_3(SO_4)_2(OH)_6$ where $M = K^+$; Na^+ ; NH_4^+ ; Ag^+ ; $\frac{1}{2}Pb^{+2}$; H_3O^+ ; etc. [3]. Some zinc, principally as zinc ferrite, is lost with the jarosite.

The jarosite residue as received was a reddish-brown bulky material. The chemical composition (determined by atomic absorption spectrometry) was 7.24 wt % Zn, 38.76 wt % Fe, and 1.61 wt % Pb. If the zinc is present as zinc ferrite $ZnOFe_2O_3$ and lead as PbSO₄ (discussed fully below) the elemental assays correspond to the composition ≈ 26.7 wt % ZnOFe₂O₃, 70.9 wt % jarosite and 2.4 wt % PbSO₄.

The size distribution was determined by Cyclosizer and X-ray diffraction (XRD) patterns of the cone fractions were taken. The patterns corresponded to those of sodium jarosite and zinc ferrite. Figure 2 indicates the approximate size distributions of the two phases, which were calculated on the assumption that all the zinc occurs as zinc ferrite and all remaining iron is in the jarosite. It can be seen that the zinc ferrite is coarser than the sodium jarosite.

Magnetic Profile and Susceptibility

The magnetic profile for the Cyclosizer cone 3 fraction was obtained on a Frantz separator [4] and is presented in Figure 3. Two distinct magnetic fractions are shown to be present corresponding to Iso values of 225 mA and 495 mA. The mineralogical characterization of these two magnetic species was performed by

XRD and SEM. The relative intensities of the two strongest diffraction lines shown in Figure 3 indicate that the more magnetic fraction is sinc ferrite and the less magnetic fraction sodium jarosite.

The magnetic susceptibility of the sinc ferrite was found to be 7.6×10^{-3} (SI units) and that of sodium jarosite 1.0×10^{-3} . The latter value is close to that reported by Todd and Finch [5] for a variety of jarosites, including a sample from Canadian Electrolytic Zinc, Ltd. Although the susceptibilities of the two phases differ, the ratio (7.5:1) is insufficient to allow more than a limited separation by magnetic means [6].

The non-magnetic at 600 mA contain some zinc ferrite and sodium jarosite as minor constituents, the main component being SiO₂. Other minor components in the +600 mA fraction were ZnS (\approx 15 wt %); FeS; Cu₂FeSnS₄ and Cu(Fe,Sn)₂S_{3.9}.

Scanning Electron Microscopy (SEM)

The division of the jarosite residue into a series of products on the Frantz aided compositional characterization of the sample.

200- to 250 mA fraction

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Figure 4 illustrates the particle type most commonly encountered in the fraction 200-250 mA. The average Zn/Fe ratio obtained by EDS was about 0.6 which approximates the Zn/Fe atomic weight ratio (0.585) for $ZnOFe_2O_3$. Copper is present in these particles at low concentrations, the EDS Cu/Fe ratio being around 0.07. Previous studies of Cottrell dust from the copper smelter [1] showed that the contained zinc-bearing ferrites had an EDS Cu/Fe ratio of about 0.9 and that they were significantly more magnetic than those discussed here. The amount of copper in the zinc ferrite appears to play an important role in its magnetic properties.

450- to 500 mA fraction

Figure 5 shows the most abundant type of particle in the 450 to 500 mA product. The morphology and spectra were characteristic of jarosites. The general jarosite formula is $M_{(1-s)}(H_3O)xFe_3(SO_4)_2(OH)_6$ where x = 0.15-0.25 [7]. Consequently the sodium content of sodium jarosites is about 3.7 wt%. This, together with the fact than Na is a light element, explains the low Na counts found by EDS.

The EDS spectra for the jarosite indicated the presence of minor amounts of copper, zinc, arsenic and lead, which X-ray mapping showed to be evenly and intimately distributed. This is in agreement with the findings of Dutrizac [7] who suggested that these elements were incorporated in the jarosite lattice. The amount of zinc incorporated in the jarosite is important since it sets the lower limit for zinc loss in the jarosite residue. The data of Dutrizac [7] and Yaroslavtsev et al [8] indicate that the zinc content of sodium jarosite is between 0.8-1.9%, depending on the composition of the leach solution. In the present study, the average Zn/Fe ratio given by EDS was 0.0916. The zinc concentration in the jarosites investigated here, therefore, is of the order of 1 wt %.

Several jarosite particles were found to have relatively high arsenic counts, suggesting that arsenic is preferentially incorporated in the precipitated jarosite. This is in agreement with the observations of Donyina [2] and of Yaroslavtsev et al [8].

+600 mA (non-magnetic) fraction

The most abundant particles in the +600 mA, non-magnetic product gave high silicon counts confirming the presence of SiO₂, which had been identified earlier by XRD. A wide variety of other particles was found, including particles of zinc sulphide and others with large EDS counts of silicon and variable counts of base

metals, suggesting the presence of complex base-metal silicates. Also found were particles with large tin counts and particles with large counts of aluminium and silicon. The presence of tin is expected, given the nature of the Kidd Creek ore [9]. The large counts of aluminium and silicon probably correspond to feldspars and other silicate minerals. [9]. Figure 6 shows a tin-bearing particle.

Magnetic Separation

Separability curve for jarosite residue

From the assays of the magnetic products of the Frantz separator a separability curve for ferrite and jarosite was constructed (Figure 7). A high degree of separability is apparent, as would be expected in view of the fact that the two phases are not intergrown.

Description of HGMS test

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HGMS tests were conducted on an Eriez HGMS model EL5-4. An expandedmetal matrix was used with diamond-shaped holes (4x8 mm) and wires of crosssectional diameter $\approx 800 \ \mu$ m. The matrix was built from disks 38 mm in diameter held in a Plexiglas cannister (stacked to touch), each being in 90° rotation to that adjacent. The total mass of the matrix was 46.6 g.

Samples of approximately 30 g were slurried with water with 0.2% Calgon as a dispersant and passed through the matrix at various settings of slurry velocity and magnetic field strength. After collection of the slurry that had passed through the unit (i.e. the non-magnetic component), the magnet was switched off and the magnetic material was flushed out and collected.

Results of HGMS tests

The grade and recovery obtained in one set of test are presented as Figure 8. Recovery increased with decreasing grade, reflecting the increased recovery of the less magnetic phase, jarosite, at increasing field strengths. SEM analysis showed that there was no difference in the chemistry of the jarosite reporting to the magnetic and non-magnetic fractions.

From Figure 8 it is apparent that the maximum zinc recovery was only 30%. The expected sources of zinc loss were zinc sulphides, complex base-metal silicates and the zinc entrapped in the jarosite structure; however, XRD analysis of the non-magnetic showed that the dominant zinc ferrite phase was zinc ferrite. Part of the loss may be attributable to fine ferrite reporting in the non-magnetics, but it is suspected that the ferrites have a variable susceptibility —perhaps related to a variable Zn/Fe ratio. SEM analysis failed to identify any difference between ferrite in the HGMS magnetic and non-magnetic fractions.

A final attempt to enhance separation by incorporating roughing and cleaning stages resulted in some improvement (Table 1) but increased circuit complexity (and cost).

STAGE	FLOW RATE	ZINC	
	cm/s	GRADE %	RECOVERY %
Rougher			
non-mags.	4	5.69	45.0
Cleaner			
non-mags	9	4.75	16.4
mags	9	14.4	38.8

Table 1. HGMS Roughing and cleaning of jarosite residue. (Field1.8T)

HOT ACID LEACH RESIDUE

Description

The HAL residue sample was a grey-black residue of specific gravity 3.1. The chemical composition, by weight, was Zn, 9.80%; Fe, 11.72%; Pb, 7.94%; and Cu, 0.60%. Size analysis established the the sample was $>80\% -10\mu m$.

Magnetic profile and susceptibility

The magnetic profile for the cone 3 fraction is presented as Figure 9. It shows an I₅₀ value of 260 mA, very nearly the same as that found for the ferrite fraction in the jarosite residue. The calculated magnetic susceptibility is 4×10^{-3} .

The Frantz separator products were assayed for zinc, iron and lead and separability curves were constructed (Figure 10). Zinc (and iron) is preferentially recovered in the magnetics whereas most of the lead reports to the non-magnetic. The separability curves demonstrate the possibility of obtaining a magnetic concentrate of zinc that is relatively free of lead.

Each separator product was studied by XRD, and an automated search-andmatch program (APD 1700, SANDMAN, Philips) being used to identify the unknown phases. Table 2 lists the phases identified in the different products in order of abundance.

Frantz	Major	Minor
Product	(more than 10%)	(less than 10%)
[mA]		
50	ZnFe ₂ O ₄	Fe ₂ O ₃
	PbCS ₃	CuS ₂ Sb
		Cu ₂ FeS ₄
		S
100	ZnFe ₂ O ₄	ZnS
	SiO ₂	Cu ₂ FeSnS ₄
	Fe ₂ O ₃	
200	ZnFe ₂ O ₄	Fe ₂ O ₃
	SiO ₂	SnO ₂
		$PbFe_6(SO_4)_4(OH)_{12}$
300	ZnFe ₂ O ₄	Fe ₂ O ₃
		ZnS
400	ZnFe ₂ O ₄	$PbFe_{6}(SO_{4})_{4}(OH)_{12}$
	Fe ₂ O ₃	Fe ₉ S ₈
500	ZnFe ₂ O ₄	
	Fe ₂ O ₃	
	SnO ₂	
600	SiO ₂	
	FeS	
	ZnFe ₂ O ₄	
	Fe ₂ O ₃	
NON-MAG.	SiO ₂	SnO ₂
	Cu ₂ FeSnS ₄	FeS
		ZnFe ₂ O ₄

Table 2. Phases identified in the hot acid leach residue by XRD (APD 1700, SANDMAN, Philips)

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Lead trithiocarbonate was tentatively identified as the lead phase in the 50 mA (most magnetic) fraction. Its occurrence could result from the presence of xanthate in the original sinc concentrate, which decomposes to free xanthogenic acid when treated with sulphuric acid [10] and may subsequently react with lead to form PbCS₃.

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It has been suspected that a major lead phase would be lead jarosite. This phase was positively identified in the 200 and 400 mA mags. The principal lead phase, however, must reside in the non-magnetic fraction which contains 5.2 wt % Pb, accounting for 60 % of the original lead in the residue. The thermodynamically stable phase from the roasters (925 °C, 6 %SO₂) is PbSO₄ (with some PbOPbSO₄), which is resistant to sulphuric acid [1] and is non-magnetic. No lead phase, however, was identified in the non-magnetic fraction. This may be accounted for by the fact that 5.2 wt % Pb represents only 7.6 wt % PbSO₄. In a synthetic mixture of 7.6 wt % PbSO₄ with 92.4 wt % SiO₂ the I₁₆₀ XRD-line of PbSO₄ gave only about 270 counts -compared with 1500 counts for pure PbSO₄. The PbSO₄ may be present but at too great dilution to be identified. On the other hand, if the 5.2 wt % Pb were present as lead jarosite, this would correspond to 28.3 wt % lead jarosite, which should produce well-defined XRD-lines.

The principal zinc phase was zinc ferrite, which is distributed throughout the magnetic profile. No silver phase was detected by XRD although silver is known [2, 7] to be present.

Scanning electron microscopy

-50 mA fraction

Figures 11 and 12 illustrate the two typical morphologies that are found in the -50 mA separator product. Representative of the first type consisted of an aggregate of small crystals and invariably contained high concentrations of iron and sinc. EDS analysis of the individual crystals gives the same spectra as those of the whole particle; both spectra correspond to zinc ferrite. The average EDS-ZAF Zn/Fe ratio of several particles was 0.37. The particle illustrated in Figure 12 —besides having large iron and zinc counts— also produced high lead and sulphur counts, which could be due to the presence of the lead trithiocarbonate identified by XRD-APD (Table 2). Thus, the -50 mA magnetic product consists of two type of particle: clean zinc ferrites and zinc ferrites agglomerated with a Pb-S compound.

The zinc ferrites from the jarosite and from the HAL residues have different morphologies. The more crystalline appearance of the zinc ferrite from the HAL may be due to the fact that such ferrites have been subjected to strong acid leaching conditions. This may indicate that zinc ferrites from the HAL residue have a decreased solubility in sulphuric acid circuits. On the other hand, zinc ferrites from the jarosite residue may be still be partly soluble in sulphuric acid and, therefore, may be recycled directly to the leaching part of the circuit.

300- to 300 mA fraction

Figure 13 illustrates the most abundant type of particle present in the 200 to 300 mA fraction. The large EDS counts of iron and zinc indicate that the particle consists of zinc ferrite. The average EDS-ZAF Zn/Fe ratio for several particles was 0.47 (0.37 for the -50 mA product). The theoretical weight per cent ratio for ZnFe₂O₄ is 0.59. The Zn/Fe ratio can probably be correlated with magnetic

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susceptibility (as it can for sinc sulphides [12]) —the higher the ratio the lower the susceptibility. The occurrence of sinc ferrite at increasing current settings, therefore, should correspond to progressively higher Zn/Fe ratios. This was difficult to prove in the present study because the number of clean sinc ferrite particles decreased markedly at higher currents. The implication is that different Zn/Fe ratios form in the roaster or that sinc is preferentially leached after formation. The proposal that sinc ferrites form by reaction on an iron oxide nucleus [1, 13] would imply that the sinc in the outer reaction layers is easily leached, giving rise to variable Zn/Fe ratios.

Like that in the jarosite residue, the ferrite in the HAL residue is significantly less magnetic than that in the Cottrell dust —which again, corresponds to a low Cu/Fe ratio (≈ 0.06 , Figures 11, 12 and 13).

Element ratios determined by EDS for other particles corresponded to hematite, and some contained appreciable manganese —possibly as a result of the MnO_2 added in the neutral leaching stage to oxidize Fe (II) to Fe (III).

+600 mA (non-magnetic) fraction

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XRD analysis of the +600 mA, non-magnetic fraction showed that 70% of the total intensity was due to SiO₂. This was confirmed by SEM, most of the particles giving EDS spectra with large silicon peaks. Figure 14 illustrates typical particles found in this product. Some other particles showed EDS spectra with large silicon peaks and significant peaks for copper, iron and zinc (Figure 15), suggesting the presence of complex base-metal silicates. Their unleachable nature in the plant circuit is indicated by their strong angular morphology (Figure 15).

Occasional particles of variable morphology were found to be rich in lead (Figure 16). The lead content (EDS-standardless analysis) varied between 78% to 57%. This supports the argument presented above that the principal lead phase in the non-magnetic product is not lead jarosite (Pb 18.3 wt%) but lead sulphate PbSO₄ (Pb, 68.3 wt%) and/or lead oxy-sulphate PbOPbSO₄ (Pb, 78.7 wt%).

HGMS —results

The equipment and conditions that were used to investigate high-gradient magnetic separation of the HAL residue were identical that those employed for the jarosite residue (above). The grade and recovery of zinc obtained for the HAL residue as a function of magnetic field strength for a flow rate of 9.7 cm/s are shown in Figure 17. Recovery increased slightly with increasing field strength, whereas the grade decreased slightly. Zinc recovery approached 30% at a grade of 20-22% Zn (corresponding to 75-80 wt% zinc ferrite). More that 98% of the lead passed to the non-magnetic fraction. For this residue, therefore, HGMS appears to be an attractive option in that it gives a clean, almost lead-free zinc ferrite concentrate.

XRD analysis of the non-magnetic fraction of the runs at 0.69T and 1.83T revealed the presence of $H_2Ca_2Zn(AsO_4)_2(OH)_2$ at an approximate concentration of 15 wt%. This phase contributes, in part, to the low recovery of zinc in the magnetic product. It was found, however, that $ZnFe_2O_4$ was still present in the non-magnetic fraction and accounts for the major zinc loss. As for the jarosite residue, the suspicion is that ferrite in the non-magnetic fraction is less magnetic because it has a higher Zn/Fe ratio.

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CONCLUSIONS

Jarosite residue

1. The evidence from XRD and SEM studies showed that the jarosite residue consisted of the following phases: most abundant —more than 10 wt %— sodium jarosite, NaFe₃(SO₄)₂(OH)₆ with small quantities of zinc, copper and arsenic incorporated in the crystal lattice; of medium abundance —from 1 to 10 wt %— zinc ferrite, ZnOFe₂O₃, and quartz, SiO₂ (in the particles of zinc ferrite, small variable amounts of copper were found); and of minor abundance —less than 1 wt % alkali feldspars (KNa)AlSi3O₈, ZnS, FeS, Cu₂FeSnS₄, Cu(Fe,Sn)₂S_{3.9} and Cu-Zn-Fe-Sn silicates.

2. Zinc ferrite is coarser than the sodium jarosite.

3. The magnetic susceptibilities of zinc ferrite and sodium jarosite in the jarosite residue were 7.6×10^{-3} and 1.0×10^{-3} respectively. The small difference limits the magnetic separation that can be achieved.

Hot acid leach residue

1. The following phases were identified in the HAL residue; most abundant --more than 10 wt %- ZnOFe₂O₃, Fe₂O₃ and SiO₂; of medium abundance --from 1 to 10 wt %- SnO₂, PbCS₃, PbFe₆(SO₄)₄(OH)₁₂, ZnS, H₂Ca₂Zn(AsO₄)₂(OH)₂, and CuS₂Sb; and of minor abundance --less than 1 wt %- MnO₂, FeS, Cu₃FeS₄, Fe₉S₈, S, and Cu₂FeSnS₄ and Cu-Zn-Fe-Sn silicates.

2. The presence of PbSO₄ is predicted on thermodynamic grounds but it was

not identified by XRD. SEM examination of the +600 mA non-magnetic from the Frantz separator revealed a few particles with a high lead content, indicating the probable presence of PbSO₄ or lead oxy-sulphates.

3. Zinc ferrite was found to be the major magnetic phase and to have a magnetic susceptibility of 4.0×10^{-3} . Lead jarosite is a minor magnetic phase.

4. HGMS separation of HAL residue at 1.8T and flow rate of 9.7 cm/s gave $\approx 25\%$ Zn recovery at a grade of $\approx 20\%$ which corresponds to $\approx 75\%$ zinc ferrite. The lead content of the magnetic fraction is <2 wt%. For this residue, therefore HGMS appears to be an attractive option since it gives a clean, almost lead-free zinc ferrite concentrate. The zinc losses to the non-magnetic may be accounted for by the presence of a zinc ferrite that is less magnetic -possibly because of a higher Zn/Fe ratio. (Similar reasoning may apply to zinc losses to that fraction in the treatment of jarosite residue.)

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Figure 1 Schematic flowsheet of zinc leaching circuit, Kidd Creek Mines, Ltd., indicating stages at which jarosite and HAL residues are generated. (From Donyina [2])

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Figure 2 Size distribution of zinc ferrite and sodium jarosite phases in jarosite residue. (Equivalent particle size based on sp. gr. zinc ferrite 5.324 and sp. gr. sodium jarosite 2.878)



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Figure 3 Magnetic profile of jarosite residue. Two profiles shown generated after splitting sample at 400 mA. Figures next to curves refer to relative intensity of diffraction lines indicated. Profiles generated on Frantz isodynamic separator with side slope 20°



Figure 4 SEM micrograph of typical ferrite particle in 200 to 250 mA Frantz separator fraction from jarosite residue. EDS peak ratios (Fe = 1): Zn, 0.62; Cu, 0.07



Figure 5 SEM micrograph of typical jarosite particle in 450 to 500 mA Frantz separator fraction of jarosite residue. EDS peak ratios (Fe = 1): Na, 0.001; S, 0.11; Cu, 0.09; Zn, 0.02



Figure 6 SEM micrograph of tin-bearing particle in the +600 mA (non-magnetic) Frantz separator fraction from jarosite residue. EDS peak ratio (Sn = 1): Si, 0.03

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Figure 7 Magnetic separability curve for zinc ferrite and sodium jarosite from jarosite residue (Cyclosizer cone (3) product)

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Figure 8 HGMS tests: zinc grade and recovery versus field strength at flow rate of 9.7 cm/s for jarosite residue

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Figure 9 Magnetic profile of HAL residue (Cyclosizer cone (3) product). Profile generated on Frantz separator with side slope 20° (I₅₀ current at which 50% of magnetics reports to the magnetic chute)



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Figure 10 Magnetic separability curves for zinc and lead phases from HAL residue (Cyclosizer cone (3) product)



Figure 11 SEM micrograph showing one of two typical particle morphologies in the -50 mA Frantz separator fraction of HAL residue. EDS peak ratios (Fe = 1): Zn, 0.35 (ZAF corrected); S+Pb, 0.15 (not ZAF corrected); Cu, 0.22 (ZAF corrected)



Figure 12 SEM micrograph showing second of two typical particle morphologies in -50 mA Frantz separator fraction of HAL residue. EDS peak ratios (Fe = 1): S+Pb, 1.04 (not ZAF corrected); Zn, 0.31 (ZAF corrected); Cu, 0.06 (ZAF corrected)



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Figure 13 SEM micrograph of typical particles in 200 to 300 mA Frantz separator fraction of HAL residue. EDS peak ratios (Fe = 1) for particle in centre: Zn, 0.47 (ZAF corrected); S+Pb, 0.09 (not ZAF corrected): Cu. 0.31 (ZAF corrected)



Figure 14 SEM micrograph of typical particles in +600 mA (nonmagnetic) Frantz separator fraction of HAL residue. EDS peak ratios (Si = 1): Fe, 0.11; Cu, 0.14; Zn, 0.08



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Figure 15 SEM micrograph of particle in +600 mA (non-magnetic) Frantz separator fraction of HAL residue with composition indicative of complex base-metal silicates. EDS peak ratios (Si = 1): Cu, 0.60; Zn, 0.5; Fe, 0.48



Figure 16 SEM micrograph of lead-rich particle in +600 mA(nonmagnetic) Frantz separator fraction of HAL residue. EDS standardless analysis gives Pb content of 78.3 wt %



Figure 17 HGMS tests: zinc grade and recovery from HAL residue versus field strength at flow rate of 9.7 cm/s

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Connecting Text for Manuscript V: Evidence of variable zinc to iron ratio in zinc-ferrites produced from roasting of zinc sulphide concentrates

The characterization of the copper smelter dust, the jarosite and the HAL residues reported in Manuscripts I to IV all showed the presence of zinc ferrite, $ZnFe_2O_4$. The combined results suggested that zinc ferrite may have a variable Zn/Fe ratio which was possibly related to its magnetic susceptibility. A systematic study to prove this variability is reported in Manuscript V. For this, a residue with higher concentrations of zinc ferrite was selected, this was the low-acid-leach residue of the Canadian Electrolytic Zinc plant.

The discussions with the reviewers for manuscript V are included since the journal where the paper was published uses such format.

Three appendixes are included at the end of Manuscript V. They are intended to provide a better explanation for some topics just mentioned in the text for Manuscript V.

MANUSCRIPT V

EVIDENCE OF VARIABLE Zn/Fe IN ZINC-FERRITES PRODUCED FROM ROASTING OF ZINC SULPHIDE CONCENTRATE

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Paper in Press: Int. Journal of Scanning Microscopy

Evidence of variable Zn/Fe in zinc-ferrites produced from roasting of zinc sulphide concentrate

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ABSTRACT

Zn-Fe-O phases formed during roasting of concentrates from zinc sulfide ores produce soluble zinc oxide, oxy-sulfates and insoluble ferrite compounds. The ferrites have a general formula $ZnOFe_2O_3$. However, these ferrites have a range of magnetic properties, suggesting variable stoichiometry. Scanning electron microscopy has been used to obtain the general relationship between the Zn/Fe ratio of the ferrites and their magnetic susceptibility.

INTRODUCTION

In preparation for leaching, zinc sulfide concentrates are roasted to form, primarily, zinc oxide which is readily soluble in sulfuric acid. During roasting zinc ferrite is also formed. Zinc ferrite is an undesirable phase because it is more difficult to leach, requiring more aggressive hot acid leaching.

In earlier papers (Lastra et al, 1987a and 1987b) the characterization of three residues from Kidd Creek all containing zinc ferrites was reported. These residues

were: 1.- Smelter dust from the Mitsubishi-copper plant; 2.- Jarosite residue and 3.- Hot-Acid-Leach (HAL) residue. The characterization of those zinc ferrites was facilitated by magnetic fractionation at different magnetic fields, producing a series of magnetic fractions. SEM-EDS analysis of of a few (<10) particles of some of the magnetic fractions of the HAL residue suggested that zinc ferrite may have a variable Zn/Fe ratio which was possibly related to their magnetic susceptibility. Because a variable Zn/Fe ratio of zinc ferrite has important metallurgical implications a systematic study was undertaken to examine the variability of the Zn/Fe ratio and its relationship to the magnetic susceptibility. This systematic study is reported here. For this study a different source of zinc ferrite was used, a residue from the Canadian Electrolytic Zinc plant, and the Zn/Fe ratio values were obtained by SEM-EDS analysis of about 100 particles from each of the magnetic fractions where zinc ferrite was found to be the most abundant phase.

SAMPLE DESCRIPTION AND PHASE IDENTIFICA-TION

The sample was a red-brown moist paste from the low-acid-leach circuit of the zinc plant of Canadian Electrolytic Zinc (CEZ) (Figure 1). The sample as received was dried at 100 °C for 24hrs and homogenized. The specific gravity of the sample was determined (conventional and gas-null picnometer) to be an average of 4.095 with a standard deviation of 0.102. The maximum particle size (determined by screening) was about 95 μ m. Size classification was performed with a Warman Cyclosizer (Kelsall and McAdam, 1963) to produce five closely sized fractions (Table 1). The Cyclosizer collects into a single cone fraction all particles which have a settling rate within a specified range. The equivalent particle size reported is the calculated diameter of spherical particles of specific gravity 4.095 with the same settling rate. The major phases were identified with an X-ray diffractometer coupled with an automated diffractometry software package (APD 1700, V3, Philips). The X-ray spectra were acquired using Cu K_{a1} and K_{a2} radiation from a copper tube operated at 40 kV and 20 mA. The scan was performed between 5 to 100 2θ -degrees with a step size of 0.020 deg. and a sampling time of 1 second.

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For elemental analysis, the samples were sprinkled on double sided adhesive tape, providing a dense coverage, and were mounted on graphite stubs. Standardless quantitative SEM-EDS analysis (SQ, Tracor TN5500) was performed using general frames at magnifications of 100X. The results of these bulk elemental analyses were used to provide the list of present elements to the automated XRD search-andmatch program, as this aids characterization using the automated search-match software.

Table 2 gives the major phases identified as present in the original sample and in the cone fractions of the cyclosizer. The approximate weight percent is only an estimate (given by the program SANDMAN) since matrix corrections were not performed. However the results do indicate the relative proportions of the major phases present in the cone fractions. Using the results in Table 2 it is possible to select cone size fractions suited for the magnetic fractionation.

Table	1.	Particle size	analysis	of the	low	acid	leach	residue	from
CI	CZ								

Cone Number	Equivalent Particle Size $[\mu m]$	Weight %
1	36.29	1.7
2	27.21	3.9
3	18.97	6.9
4	12.37	7.5
5	9.07	5.4
-5	-9.07	74.60

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Table 2. Major phases identified by SANDMAN-APD 1700 in the original low-acid-leach residue CEZ sample and in the size fractions from the Cyclosizer.

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SAMPLE	IDENTIFIED PHASE		
	FORMULA	APPROXIMATE	
		wt. %	
original	ZnFe ₂ O ₄	80	
	Fe2O3	7	
	PbSO4	5	
cone 1	ZnFe ₂ O ₄	81	
	Fe ₂ O ₃	4	
	FeS ₂	4	
cone 2	ZnFe ₂ O ₄	64	
	Fe ₂ O ₃	12	
	ZnS	12	
cone 3	ZnFe ₂ O ₄	78	
	Fe ₂ O ₃	12	
cone 4	ZnFe ₂ O ₄	45	
	Fe_2O_3	14	
	ZnS	37	
	SiO ₂	5	
cone 5	ZnFe ₂ O ₄	71	
	Fe_2O_3	20	
-cone 5	ZnFe ₂ O ₄	95	
	Fe ₂ O ₃	5	

PHASE SEPARATION ON FRANTZ ISODYNAMIC MAGNETIC SEPARATOR

Magnetic fractionation of the ferrites was performed on an isodynamic separator(Frantz). This unit achieves precise separation based solely on differences in magnetic susceptibilities (Hess, 1959). Magnetic separation on the Frantz is performed dry and is best on relatively coarse (>15 μ m) mono-sized fractions. From Table 2 it can be seen that of the coarse size fractions, cone 3 has the simplest

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major-phase composition where sinc ferrite is the most abundant phase. Therefore the cone 3 fraction was selected for magnetic fractionation.

The procedure consisted of separating the sample into magnetics and nonmagnetics at a given current on the Frants. The sample was fed slowly and evenly by a vibrator to approach separation on a particle-by-particle basis. Typically the feed rate was such that a 1-gram sample took 3 days to process. When all the sample was passed, the magnetics were weighed and stored while the non-magnetics were used as feed for a higher current setting. Table 3 shows the results for the separations performed at currents 20 to 572 mA. The equivalent magnetic field given in Table 3 was obtained from previous calibrations of the Frantz (Nesset and Finch, 1980). The magnetic susceptibility in Table 3, was calculated from (Hess, 1959; Dobby et al, 1979; Finch and Leroux, 1982):

$$\mathcal{K} = \frac{\delta_P \, 2.5 \times 10^{-7} \, \sin \theta}{I^2} \tag{1}$$

where:

 \mathcal{K} = Magnetic susceptibility [S.I. units] δ_p = Particle Density $[Kg/m^3]$ θ = Side slope of Frantz unit [deg] I = Current to the magnet [A]

An average susceptibility corresponds to that giving a 50:50 split of the magnetic material. In this case since the sample contained about 76% of magnetic material (the percent separating to magnetics above \approx 470 mA was negligible) then 50% of the magnetic fraction is at \approx 38% mass recovery and by interpolation from Table 3, $K \approx$ 8×10⁻³. This value is similar to that reported for zinc ferrite from the Kidd Creek jarosite and HAL residues. (Lastra et al, 1987b).

CURRENT	EQUIVALENT	EQUIVALENT	WEIGHT	CUMULATIVE
to the	MAGNETIC	MAGNETIC	%	WEIGHT
MAGNET	FIELD	SUSCEPT.		%
[mA]	[T]	[S.I.]		
		units		
20	0.03	8.75x10 ⁻¹	0.14	0.14
40	0.06	2.19×10^{-1}	5.09	5.23
80	0.11	5.47x10 ⁻²	5.75	10.98
130	0.18	2.07x10 ⁻²	9.75	20.73
180	0.25	1.08x10 ⁻²	8.92	29.65
211	0.29	7.86x10 ⁻³	16.15	45.80
250	0.34	5.60x10 ⁻³	1. 69	47.49
300	0.41	3.89x10 ⁻³	15. 05	62.54
356	0.49	2.76x10 ⁻³	7.56	70.10
412	0.57	2.06x10 ⁻³	4.67	74.77
476	0.66	1.55x10 ⁻³	0.39	75.16
572	0.79	1.03x10 ⁻³	1.09	76.25

Table 3. Frants magnetic separation of cone 3 fraction of CEZ ferrites. Frants side slope was 20°

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XRD OF MAGNETIC PRODUCTS

The Frantz magnetic products were studied by XRD using a similar procedure to that already described. Table 4 gives the identified major phases. It can be seen that the magnetic products up to 412 mA are mainly binary mixtures. The concentration of the two phases in these products was calculated from the following (Chung, 1974):

$$X_1 = \frac{1}{1 + (k_1/k_2)(I_2/I_1)}$$
(2)

where:

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 X_1 = weight fraction of phase 1 $k_i = I_i/I_c$

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- I_i = intensity of a selected line of phase "i" in a 50-50 mixture with corundum
- I_c = intensity of a selected line of corundum in a 50-50 mixture with phase "*i*"
- I_1 = intensity of the same selected line, phase 1 in the unknown binary
- I_2 = intensity of the same selected line, phase 2 in the unknown binary

The values used for ki were the I/Ic figures published by JCPDS, consequently the results are approximate. However, they are more accurate than the ones given by program SANDMAN since eq. 2 allows for some matrix correction. Table 4 shows that the concentration of zinc ferrite is high in the magnetics up to 211 mA, then the concentration decreases; in the magnetics of 356 and 412 mA the most abundant phase is hematite.

SEM OF MAGNETIC FRACTIONS

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The SEM study was designed to measure the Zn/Fe ratio of particles in the Frantz fractions to determine if the wide range in susceptibility (Table 3) was related to the Zn/Fe ratio, as previous work had suggested (Lastra et al, 1987b).

Frantz fractions up to 300 mA were used, as these contain primarily zinc ferrite (Table 4). However, they also contain other iron phases, thus the Zn/Fe ratio cannot be measured by bulk analysis. The SEM-EDS technique, therefore, was used to measure the Zn/Fe ratio on a particle-by-particle basis. About 70-100 particles in each Frantz fraction were examined. The sample preparation method was to sprinkle on double side adhesive tape mounted on a graphite planchette. This simple sample preparation method was made possible due to the relatively coarse particle size (cone 3 size fraction).

Quantitative X-ray microanalysis is complicated by geometric effects (Goldstein, 1981). The complications can be divided into mass effects, absorption effects and fluorescence effects. The mass effect arises when the particle dimensions are equal or smaller than the interaction volume. This effect is limited by using cone 3 size particles. The absorption effect was alleviated by using a high-take-off angle to the detector of 53° and by scanning the whole particle (i.e. bracketing) when acquiring EDS spectra. Some inaccuracy can be expected due to the rough surface of the particles. Polished specimens will not significantly reduce this effect as the particles are not solid but aggregates of fused crystallites, which makes polishing difficult due to plucking out of crystallites from the sample.

The program VISTA-SIA (TRACOR TN500, series II) was used to simplify the task of accumulating information. A working frame of approximately 350X was used in order to have sufficient particles per frame while still maintaining a good

resolution of the particles. The selection of the cone 3 size fraction also allowed the use of low magnifications. Figure 2 shows a typical working frame for the 40 mA magnetic fraction. The working frame was transformed into a digital image (512x512 pixel) using the video signal. The digitized image was used to create a binary image depicting those pixels which belong to particle-areas. This binary image was edited to separate touching particles and to close pixel holes inside the particles (Figure 3). The binary image was used as a template to guide the electron beam to the particles and do bracketing EDS acquisition for 30 seconds. Figure 4 is a 3-minute exposure photograph of the SEM screen showing the dot-matrix used for the electron beam to perform bracketing scans for each particle. Figure 5 is a photograph of the TRACOR screen while the particles in the frame are being characterized by size and by chemical type. Sufficient working frames were used to include approximately 100 particles per magnetic fraction. The particles were classified by the program into chemical type by considering the associations and the normalized-percent counts in the EDS windows of Zn, Fe, Cu, Si, Al, S, Cd, and Pb. Typically all particles could be classified by the defined element-windows.

It was found that the magnetic fractions up to 300 mA contained a majority of particles having at least 94% of their normalized counts due to iron plus zinc (i.e. zinc ferrites, in agreement with the XRD results in Table 4). The normalizedpercent counts for zinc and iron were used to plot histograms and to obtain the most frequent (modal) Zn/Fe ratio. This ratio was then ZAF-corrected to calculate what was called the modal EDS-ZAF Zn/Fe ratio.

Figure 6 shows a zinc ferrite which has the modal EDS-ZAF Zn/Fe ratio of 0.36 for the 40 mA magnetic fraction. Figure 7 shows a zinc ferrite particle in the 300 mA fraction with the EDS-ZAF Zn/Fe ratio of 0.53. No obvious differences in morphology between the particles is apparent despite the difference in Zn/Fe ratios. Figure 8 shows a BE image of the particle in Figure 7. It is clear that these particles are of heterogeneous nature. This is another justification for using full

particle scanning to obtain the EDS spectra.

Figure 9 summarises the observations, it gives the modal Zn/Fe ratio found in each magnetic fraction. The lower curve gives the modal Zn/Fe ratio not ZAF corrected while the upper curve gives the same ratio but ZAF-corrected. The bars in Figure 9 are for plus/minus one standard deviation. It can be seen that the mode Zn/Fe ratio (ZAF or not ZAF corrected) tend to increase in the magnetic fractions obtained at higher currents (those which have lower magnetic susceptibility). The EDS-ZAF Zn/Fe ratio increases up to about 0.55 for the magnetic fraction of 180 mA, then remains approximately constant up to 211 mA. The ratio of ≈ 0.55 is close to the stoichiometric value of 0.59 for ZnOFe₂O₃. The Zn/Fe ratio decreases slightly for the magnetic fractions of 250 and 300 mA.

DISCUSSION

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Figure 9 was constructed using the modal Zn/Fe ratio. The latter was obtained from histograms of normalized percent counts for zinc and iron. The histograms showed scatter. This scatter may be partly due to geometrical effects or the presence in the magnetic fractions of particles that have been mechanically misplaced in the Frantz separator. Therefore the mode was used because it has the advantage, over the mean, of eliminating outlier data

The EDS modal Zn/Fe ratios were all ZAF corrected for easy comparison with the stoichiometric weight percent Zn/Fe ratio of ZnOFe₂O₃. As it is known that the particle geometry affects ZAF corrections the experiment was designed to alleviate geometrical effects. For example the use of a high take-off angle, the bracketing raster on the whole of the particle, and their relatively coarse size are all factors that reduce the geometrical effects. Also, employing many particles to obtain the mode Zn/Fe ratio reduces the bias from geometrical effects because many particle-orientations are included. However, it is recognized that the results of the EDS-ZAF correction may not be absolute, but the importance is in the trend of the Zn/Fe ratio with magnetic susceptibility. Figure 9 shows that even the uncorrected mode Zn/Fe ratio exhibits larger values for the fractions obtained at higher currents. Therefore it is well demonstrated that the Zn/Fe ratio tends to increase as magnetic susceptibility decreases.

Table 4 shows that the only zinc-containing phase in the magnetic fractions up to 300 mA is zinc ferrite. The stoichiometric ratio for $ZnOFe_2O_3$ is 0.59, yet despite the absence of any other zinc-containing phase the Zn/Fe ratio varies from ≈ 0.35 to ≈ 0.55 . The following possibilities could explain such a variation:

- 1.-The agglomerate nature of the particles may mean stoichiometric zinc ferrite is present with stoichiometric hematite. The presence of hematite will lower the Zn/Fe ratio of the agglomerate.
- 2.-Magnetite (Fe₃O₄), as a separate phase, may be also present in the agglomerates. This could also lower the Zn/Fe ratio of the aggregates.
- 3.-Zinc ferrite has a compositional variation which is related to changes in magnetic susceptibility.

The first possibility can be discarded because stoichiometric hematite has a lower magnetic susceptibility than stoichiometric zinc ferrite (Taggart, 1954 and Telford et al, 1978). Therefore agglomerates having larger proportions of hematite (and hence lower Zn/Fe ratio) should report to magnetic fractions having lower magnetic susceptibility and not as indicated in Figure 9 to magnetic products having higher magnetic susceptibility.

The second possibility does correspond to the correlation between Zn/Fe ratio and magnetic susceptibility since stoichiometric magnetite has a higher magnetic susceptibility than stoichiometric zinc ferrite. The fact that XRD did not identify magnetite as a major present phase is not enough to eliminate this possibility since the XRD patterns of zinc ferrite and magnetite are similar (Figure 10) and the automated search and match program may not be able to distinguish the two phases.

However, the second possibility does require magnetite to be a thermodynamically stable phase under the conditions of the roasting of zinc sulphide concentrates, which is not the case (Benner and Kenworthy 1966). Subsequent Mössbauer spectroscopy on these samples supported that magnetite is not present (paper in preparation, Muir et al. 1988 [186]). Therefore the second possibility can be rejected.

The results are best explained by zinc ferrites with compositional variation. The compositional variation leads to variable magnetic susceptibility. The lower the Zn/Fe ratio the higher the susceptibility. The compositional variation of the zinc ferrites and the XRD results support a solid solution ferrite of the form $Zn_zFe_{3-z}O_4$ whose crystal dimensions change little, making the automated XRD search and match program identify zinc ferrite (ZnOFe₂O₃). The proposal agrees with the reported behaviour for synthetically prepared zinc ferrites: Lyamina et al, 1985 identified by electron diffraction analysis, a solid solution $Zn_zFe_{3-z}O_4$ with a lattice parameter (a_0) varying continuously between stoichiometric zinc ferrite and magnetite with $a_0=0.8390$ nm at x=1 and 0.8437 nm at x=0. (Figure 10 indicates the similarity of the XRD patterns of $ZnFe_2O_4$ and Fe_3O_4); Srivastava et al, 1976, prepared synthetic zinc ferrites from pure ZnO and Fe_2O_3 , they found that the magnetization at 303 K decreased with increasing zinc concentration for zinc ferrites with x=0.2 to x=0.8 for $Zn_zFe_{3-z}O_4$ (corresponding to Zn/Fe wt% ratio of 0.18 to 0.43 respectively).

It is believed that the variable Zn/Fe ratio of the industrially produced ferrites could also have an influence on their leachability. There is a suspicion that the lower Zn/Fe ratio ferrites are harder to leach. Since there is a possibility of recovering ferrites magnetically for recycling, this will preferentially recycle low Zn/Fe ratio ferrites which, if the suspicion is founded, is not desirable. Experimental evidence is necessary to test the leachability of the zinc ferrites as a function of their Zn/Feratio.

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Finally, the slight decrease of the Zn/Fe ratio for the magnetic fractions of 250 and 300 mA might be explained by the fact that the hematite content of these fractions increases up to \approx 33%. This increases the chances of encountering, in these low-magnetic susceptibility fractions, agglomerates which have their Zn/Fe ratios reduced due to the presence of hematite.

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SAMPLE	IDENTIFIED	PHASES
	FORMULA	APPROXIMATE wt. %
20	ZnFe ₂ O ₄	80.3 *
	Fe ₂ O ₃	19.7 *
40	ZnFe ₂ O ₄	86.2 *
	Fe ₂ O ₃	13.8 *
80	ZnFe ₂ O ₄	84.3 *
	Fe ₂ O ₃	15.7 *
130	ZnFe ₂ O ₄	80.0 *
	Fe ₂ O ₃	20.0 *
180	ZnFe ₂ O ₄	80.7 *
	Fe ₂ O ₃	19.3 *
211	ZnFe ₂ O ₄	89.0 *
	Fe ₂ O ₃	11.0 *
250	ZnFe ₂ O ₄	67.4 *
	Fe_2O_3	32.6 *
300	ZnFe ₂ O ₄	66.9 *
	Fe ₂ O ₃	33.1 *
356	$ZnFe_2O_4$	22.3 *
	Fe ₂ O ₅	77.7 *
412	ZnFe ₂ O ₄	12.6 *
	Fe ₂ O ₃	87.4 *
476	SiO ₂	46**
	ZnAi2O4	26 **
	·ZnFe ₂ O ₄	12 **
	Fe_2O_3	15 **
572	SiO ₂	28 **
	ZnAl2O ₄	37 **
Non-Mag.	ZnS	48 **
of	FeS	36 **
572 mA	SiO ₂	11 **
	ZnFe ₂ O ₄	1 **

Table 4. Major phases identified in the Frantz magnetic products.

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* Calculated by eq. 2 ** Given by SANDMAN

CONCLUSIONS

The mode EDS-ZAF Zn/Fe ratio of zinc ferrite particles formed on roasting was not constant but changed from 0.35 to 0.55. This corresponded to a magnetic susceptibility change from $\approx 5.5 \times 10^{-2}$ to $\approx 3.9 \times 10^{-3}$ (S.I. units). The variation in the Zn/Fe ratio of the zinc ferrite is explained by a solid solution Zn_zFe_{3-z}O₄. The role of variable Zn/Fe ratio on ferrite leachability must be considered in evaluating the magnetic recovery and recyling of ferrites.

ACKNOWLEDGEMENTS

The authors wish to thank the Natural Sciences and Engineering Research Council (Strategic Grants Program) and the Ministère de l'Education du Québec (FCAR program) for financial support; the Noranda Research Centre for providing samples of CEZ plant residue; and Prof. W.B. Muir from the Physics Department of McGill University for helpful discussions.



Figure 1 General flowsheet of the CEZ plant. (Rodier, 1981). The sample for these studies was the low-acid-leach residue

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Figure 2 Sample of the 40 mA magnetic product from the cone 3 size fraction of the low-acid-leach residue of CEZ. Photograph of SEM display, showing the general type of "working frame" used for VISTA-SIA. Magnification is 350X. The area between the lines gives the area depicted in Figure 3



Figure 3 Photograph of the analyzer display showing part of the edited binary image from Figure 2. Touching particles have been separated, this allows the collection of EDS spectra from each particle, otherwise one EDS spectra from each group of particles will be collected.



Figure 4 Photograph of the SEM display while VISTA-SIA is controlling the electron beam to obtain the X-ray spectras by scanning the entire area of features of interest. Scans on six particles are shown, labels A, B, ...etc, refer to the same labels in Figure 5. <u>о</u>ч



Figure 5 Photograph of the analyzer display while VISTA-SiA is characterizing by size and chemical type the particles of the edited binary (at left) image from Figure 2. The EDS spectra shown corresponds to the last particle being analyzed (label L). The largest peak is Fe K_a, the second larger peak is Zn K_a.



Figure 6 Zinc-ferrite particle in the 40 mA magnetic product from the ferrites of the CEZ plant. ZAF-EDS Zn/Fe ratio is 0.36





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Figure 8 BEI of zinc ferrite particle in Figure 7. It can be seen that the particles analyzed in this work are in fact aggregates of smaller particles. Consequently EDS spectra acquired on the whole surface feature make results easier to interpret than EDS spectra acquired with spot analysis.



Figure 9 ZAF corrected mode Zn/Fe ratio and uncorrected mode Zn/Fe ratio for the Frants magnetic fractions of up to 300 mA. It is evident that lower Zn/Fe ratio are related to magnetic fractions obtained at lower currents. The Zn/Fe ratio for the magnetic fraction of 20 mA is not reported because it was considered unreliable due to the small amount of this fraction. At the other end, the mode Zn/Fe ratio for the fractions above 300 mA is not reported in this Figure since according to XRD, Fe₂O₃ is the major phase in those fractions.



Figure 10 XRD patterns of zinc ferrite and magnetite. The similarity of the spectra is obvious.

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DISCUSSION WITH REVIEWERS

Reviewer 1: The magnetic separation techniques, and consequently the equivalent magnetic susceptibilities are doubtful. The doubtful results can be seen from Table 4 (used to construct Figure 9, which summarizes the whole study) SiO₂ was separated at lower current than ZnS and FeS —a result that the reviewer does not believe correct.

Authors: Figure 9 was constructed with data from Table 3 and 4 for the magnetic fractions from 40 to 300 mA. The remarks concerning SiO₂, ZnS and FeS are applicable for currents of 476 mA and greater (in Table 4). These data were not used in constructing Figure 9. Independent magnetic measurements with a Foner magnetometer with the magnetic fractions (of Table 3 or 4), showed that indeed there is a large change in magnetic susceptibility, for example the values of the magnetization relative to the magnetization of nickel (M/MNi) for the fractions of 20, 40... and 211 mA are 0.51, 0.31 and 0.007 respectively. The magnetic separation technique employed, namely the Frantz separator, is the only device known to the authors that is capable of isolating fractions with only small differences in magnetic susceptibility. The Foner measurements supports the ability of the Frantz to so fractionate. As regards the SiO_2 : only part of the SiO_2 present in Cone 3 was separated at a current of 476 mA, most of it (\approx 15 times more than the SiO₂ in the 476 mA fraction) is still reporting to the non-magnetics of 572 mA. The fact that some SiO₂ reports to the 476 mA magnetic fraction, should not be considered as an obvious error raising concerns about the validity of the magnetic techniques since even slight contamination of the SiO₂ with iron increases its magnetic susceptibility (converting it from diamagnetic to paramagnetic for instance). The ZnS (pure) and FeS (especially pyrite FeS₂) are also very weakly magnetic and not readily

isolated even from SiO₂.

REVIEWER 1: There are many more compounds in the low-acid-leach residue than those listed in Table 2 and Table 4. Where are these compounds in the Frantz magnetic products?. This discrepancy exemplifies the poor quality of the quantitative XRD results.

AUTHORS: Tables 2 and 4 list only the major phases present which are all of concern here. Mössbauer analysis of selected magnetic fractions of 80 mA, 130 mA and 356 mA do show that they contain mainly zinc ferrite and Fe_2O_3 in proportions that agree with those quoted in Table 4. The Foner magnetometer and the Mössbauer measurements will be presented and discussed in a future gaper.

REVIEWER 1: It is a total supprise to the reviewer that the authors used EDX analyses on rough particles to determine the Zn/Fe wt. ratios instead of using electron microprobe on polished section mounts.

AUTHORS: Our problem was that the particles that were studied in this paper were agglomerates. The agglomerate nature of the particles is evident in Figure 8. The preparation of flat specimens involves polishing which could remove parts of those agglomerates; this would alter the samples in unknown ways. Instead of dealing with possible unknown sample preparation artifacts, it was considered more prudent to use substrate specimens to maintain the agglomerate integrity. Some precautions were taken (mentioned in the text) to reduce errors in analyzing the particles by EDS. However it is appreciated that the use of substrates and SEM-EDS would mean more inaccurate Zn/Fe values. However, absolute accuracy of the Zn/Fe ratios could be sacrificed since the objective of the work was to find the general trend between the Zn/Fe ratio and the magnetic susceptibility in the industrially produced zinc ferrites. The results of this paper show conclusively that the industrially produced zinc ferrites have a variation in magnetic susceptibility which is related with a variable Zn/Fe ratio, the lower Zn/Fe zinc ferrites showing higher values of susceptibility. These results, interestingly, are in agreement with the findings relating variation in composition and magnetic properties of synthetically produced zinc ferrites (Srivastava et al, 1976).

REVIEWER 1: If zinc ferrite has a compositional variation, its cell dimension should show linear variation with composition. A careful X-ray diffraction study, such as least-square cell refinements from X-ray powder data should show the variations.

AUTHORS: As mentioned in the text zinc ferrite does show a compositional variation. The variation in cell dimensions has been reported by others using samples better suited to that task: Lyamina et al, 1985 studied zinc ferrites prepared under laboratory conditions and identified a solid solution $Zn_{z}Fe_{3-z}O_{4}$ with lattice parameters (from electron diffraction studies) $a_{o}=0.8390$ nm at x=1 and 0.8437 nm at x=0. Srivastava et al, 1976 prepared zinc ferrites $Zn_{z}Fe_{3-z}O_{4}$ from ZnO and Fe₂O₃. They determined the lattice constant using single crystals of $Zn_{z}Fe_{3-z}O_{4}$ and found $a_{o}=0.8429$ at x=0.8 and 0.8390 nm at x=0.

The determination of the cell parameters using the agglomerates particles studied in the present paper would be unnecessarily complex. As mentioned in the text, there was scatter in the Zn/Fe ratios on a particle-by-particle basis for each magnetic fraction. It is not possible to ignore the fact that some of the scatter in the Zn/Fe ratio may be explained by particles being mechanically mis-sorted in the Frantz. The use of the mode Zn/Fe ratio has the advantage of eliminating outlier data. However using a bulk x-ray diffraction technique to obtain the variation in cell dimensions (a change from ≈ 0.839 nm to ≈ 0.843 nm) will give the values for all the zinc ferrites (even those mechanically misplaced) in the magnetic fractions. Therefore this will necessitate the use of a particle-by-particle technique to obtain the cell dimensions; i.e. collection of electron diffraction patterns on a particle by particle basis, and then obtaining the most often encountered cell parameter

(the mode a_0). This task is even more complicated if is is considered than in order to increase the perfection of the magnetic separation we use coarse "particles" ($\approx 45 \mu$ m). Electron diffraction patterns from such particles will necessitate the use of special sample preparation techniques (impregnation?, microtomy? polishing? ion polishing?). This was outside the stated scope of the work.

Finally, it is believed that the experimental results shown in the present paper together with the reported (Lyamina et al, 1985 and Srivastava et al, 1976) behaviour of synthetic zinc ferrite give enough conclusive evidence to state that the magnetic susceptibility of industrially produced zinc ferrites is related to compositional variation. In general, the lower Zn/Fe ratio the higher the magnetic susceptibility.

G. Bonifazi: Taking under consideration only 100 grains of one part of the fraction (number 3) among those obtained working the original sample, does it represent a sort of "limitation" with respect to the extension of results to the Zn-ferrites present inside the sample?. Have other surveys been carried out with reference to other fractions? If they have been, do the obtained results agree with those in this paper?

AUTHORS: The cone 3-size fraction was further fractionated magnetically. Then ≈ 100 particles of each magnetic fraction (having zinc ferrite as major phase) were examined to obtain the mode Zn/Fe ratios. Therefore in total ≈ 680 particles of cone 3-size fraction were analyzed. On the other hand it is true that only cone 3-size fraction was studied by magnetic fractionation, and SEM-EDS analysis. However, there is no reason to believe that the zinc ferrites in those size fractions would show a different trend between magnetic susceptibility and Zn/Fe ratio.

G. Bonifazi: The authors speak of "no obvious differences in morphologies between particles", but the type of morphological research carried out on the particles is not clear. The only data can be obtained from the examination of the figures. So, did you come to the conclusion that the morphology between one grain and another does not change, on the basis of a series of visual observations or of precise morphological surveys (shape analysis)? Which one? Has the same type of observation been carried out for other grain fractions? Are the obtained results the same? Which is the meaning of the "shape factor", shown in Figure 5?

AUTHORS: The "shape factor" in Figure 5 is given by the ratio $(Perimeter)^2/4Area\pi$ for each particle. However these data were not used to reach any kind of morphological conclusion. Our observations were merely of a visual nature, based upon previous experience. For example Figures 11 and 12 (Lastra et al, 1987b) show the type of zinc ferrites found in the hot-acid-leach residue of Kidd Creek, at the 50 mA fraction and at the 200 mA magnetic fraction. The change in morphology in those two figures is obvious. This type of obvious differences in morphology was not observed in the zinc ferrites at the different magnetic fractions from the cone 3-size fraction of the low-acid-leach residue of the CEZ plant.

G. Remond: How did you obtain the reference X-ray intensities used to normalize the intensities being characteristic of the particles (external standards or calculated data including the response function of the spectrometer)?

AUTHORS: Normalization (with respect to reference intensities) was done using program SQ (Tracor). This program uses references stored in computer memory. It also uses operational parameters such as the accelerating voltage and take-off angle to calculate the correction factors.



Figure 11 SEM micrograph showing one of two particles morphologies in the 50 mA Frantz separator fraction of HAL residue. EDS peak ratios (Fe=1): Zn,0.35; S+Pb,0.15; Cu,0.22



Figure 12 SEM micrograph of typical particles in the 200 mA Frantz separator fraction of HAL residue. EDS peak ratios (Fe=1) for particle in centre: Zn,0.47; S+Pb,0.09; Cu,0.31

APPENDIX 1 FOR MANUSCRIPT V ZAF-Correction of the Mode Zn/Fe Ratios

The work described in Manuscript V indicates that the mode Zn/Fe ratios of the zinc ferrite fractions with different magnetic susceptibilities were ZAF-corrected. This appendix describes how this correction was performed.

Table 1-AP1Uncorrected mode Zn/Fe ratios for the magnetic
fractions with major proportions of zinc ferrite.

Current to the Magnet [mA]	Equivalent Magnetic Susceptibility [S.I. units]	Uncorrected Mode Zn/Fe ratio	Approximate phase analysis from Table 4 [%]	
			ZnFe ₂ O ₄	Fe ₂ O ₃
40	2.19×10 ⁻¹	0.123	86.2	13.8
80	5.47×10 ⁻²	0.123	84.3	15.7
130	2.07×10^{-2}	0.185	80	20
180	1.08×10 ⁻²	0.214	80.7	19.3
211	7.86×10 ⁻³	0.214	89	11
250	5.60×10 ⁻³	0.21	67.4	32.6
300	3.89×10 ⁻³	0.20	66.9	33.1

Table 1-AP1 shows the uncorrected mode Zn/Fe ratios that were ZAF-corrected to compare with the weight-percent basis Zn/Fe ratio of stoichiometric zinc ferrite (i.e. Zn/Fe=0.59 for $ZnFe_2O_4$)

The mode Zn/Fe ratios were obtained from the Zn/Fe ratios of individual particles which contained sinc and iron only. The program (VISTA-SIA, Tracor) used to collect the data gives the normalized counts for a window of constant width inside the EDS peaks of sinc and iron. Therefore, the Zn/Fe ratio for the particles is:

$$\frac{I_{\overline{g}n}^{\overline{u}} + I_{\overline{p}e}^{\overline{u}}}{I_{\overline{g}n}^{\overline{u}} + I_{\overline{p}e}^{\overline{u}}} = \frac{I_{\overline{g}n}^{\overline{u}}}{I_{\overline{p}e}^{\overline{u}}} \qquad (1 - AP1)$$

where:

$$\frac{I_{g_n}^w}{I_{g_n}^w + I_{F_e}^w} = \text{normalized counts of zinc}$$
$$\frac{I_{F_e}^w}{I_{g_n}^w + I_{F_e}^w} = \text{normalized counts of iron}$$

and:

 I_{Zn}^{w} = counts for the window under the Zn K α EDS peak I_{Fe}^{w} = counts for the window under the Fe K α EDS peak

Therefore the question is to obtain the ratio wt $\%_{Zn}$ /wt $\%_{Fe}$ from the values of I_{Zn}^{w}/I_{Fe}^{w} .

The ZAF method gives the weight-percent by multiplying the normalized Kratios with the ZAF correction factor:

$$wt\%_i = k_i (ZAF)_i \qquad (2 - AP1)$$

where:

$$wt\%_i$$
 = weight percent of element "i"
(ZAF)_i = ZAF correction factor for element "i"

From equation 2 it can be seen that the Zn/Fe ratio on basis of weight percent

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$$\frac{wt\%_{Sn}}{wt\%_{Fe}} = \frac{k_{Sn} (ZAF)_{Sn}}{k_{Fe} (ZAF)_{Fe}} \qquad (3 - AP1)$$

The normalized K-ratios are given by:

$$k_{g_{n}} = \frac{\frac{I_{g_{n}}^{A}}{I_{g_{n}}^{A}}}{\frac{I_{g_{n}}^{A}}{I_{g_{n}}^{A}} + \frac{I_{p_{e}}^{A}}{I_{p_{e}}^{A}}} \qquad (4 - AP1)$$

$$k_{p_{e}} = \frac{\frac{I_{p_{e}}^{A}}{I_{g_{n}}^{A}} + \frac{I_{p_{e}}^{A}}{I_{p_{e}}^{B}}}{\frac{I_{g_{n}}^{A}}{I_{g_{n}}^{A}} + \frac{I_{p_{e}}^{A}}{I_{p_{e}}^{B}}} \qquad (5 - AP1)$$

where:

$$I_i^A = \text{Area under the } K_{\alpha}\text{-peak due to}$$

$$element "i"$$

$$I_i^{A,*} = \text{Reference intensity, area under the}$$

$$K_{\alpha}\text{-peak due to element "i" for a}$$
sample with known concentration
of "i".

From eqs. 4 and 5, it can be seen that the normalized K-ratio is:

$$\frac{k_{\mathbb{Z}n}}{k_{\mathbb{P}e}} = \left[\frac{I_{\mathbb{Z}n}^{\mathbb{A}}}{I_{\mathbb{F}e}^{\mathbb{A}}}\right] \times \left[\frac{I_{\mathbb{F}e}^{\mathbb{A},*}}{I_{\mathbb{Z}n}^{\mathbb{A},*}}\right]$$
(6 - AP1)

The window width used with the program VISTA-SIA was maintained constant, being the same, even for different magnetic fractions. Therefore the following equation can be stated:

$$\frac{I_{g_n}^{\omega}}{I_{F_e}^{\omega}} \times C_1 = \frac{I_{g_n}^A}{I_{F_e}^A} \qquad (7 - AP1)$$

Substituting 7 in 6:

$$\frac{k_{g_n}}{k_{p_e}} = \frac{I_{g_n}^{u}}{I_{p_e}^{w}} \times C_1 \times \frac{I_{p_e}^{A,*}}{I_{g_n}^{A,*}} \qquad (8 - \text{AP1})$$

The reference intensities may be considered constant since the acceleration voltage and the take-off angle were maintained constant for all the SEM-studies related with Manuscript V; therefore; equation 8 becomes:

$$\frac{k_{Zn}}{k_{Pe}} = \frac{I_{Zn}^{u}}{I_{Pe}^{u}} \times C_1 \times C_2 \qquad (9 - AP1)$$

or:

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$$\frac{k_{Sn}}{k_{Fe}} = \frac{I_{Sn}^{w}}{I_{Fe}^{w}} \times C_3 \qquad (10 - \text{AP1})$$

Substituting eq. 10 in eq 3:

$$\frac{wt \mathscr{K}_{g_n}}{wt \mathscr{K}_{F_e}} = \frac{I_{g_n}^w}{I_{F_e}^w} \times C_3 \times \frac{(ZAF)_{g_n}}{(ZAF)_{F_e}}$$
(11 - AP1)

The ZAF correction factor is the product of three correction factors, the absorption factor A, the fluorescence correction factor F, and the so-called atomic number factor Z. Equations are given in the literature to calculate the factors Z, A, and F. [e.g. 143]. However because of the small changes in composition involved in the zinc ferrites of different magnetic susceptibilities, then the ZAF correction factors may be considered as constant; then eq 11 becomes:

$$\frac{wt\%_{Zn}}{wt\%_{Fe}} = \frac{I_{Zn}^{w}}{I_{Fe}^{w}} \times C_4 \qquad (12 - \text{AP1})$$

Equation 12 is an equation of a linear-type:

$$Y = mX + b \tag{13-AP1}$$

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$$\frac{wt\%_{Zn}}{wt\%_{Fe}} = m \frac{I_{Zn}^{w}}{I_{Fe}^{w}} + b \qquad (14 - AP1)$$

To obtain the parameters of eq. 14 the program SQ-Tracor was used. The pro-

gram SQ is a semi-quantitative analysis program that uses reference intensities in memory. SQ uses the normalized K-ratios to calculate the correction factor $(ZAF)_i$ and with them the weight percent composition (wt $\%_i$) is given. Some sinc-ferrite particles in the different magnetic fractions were analysed by SQ. Care was taken to include particles covering the whole range of interest. (see column 3, Table 1-AP1). Table 2-AP1 shows the obtained data, and Figure 1-AP1 shows the plot of the weight percent ratio (wt $\%_{Zn}/wt \%_{Fe}$) vs. the window- ratio (I_{Zn}^w/I_{Fe}^w) . It can be seen that the data follow a linear fit well. This proves that the assumptions made to derive eqs 12 or 14 were correct. Therefore the normalized window ratio (I_{Zn}^w/I_{Fe}^w) given in the output of VISTA-SIA can be transformed to the weight percent ratio (wt $\%_{Zn}/wt \%_{Fe}$) using the following simple linear equation:

$$\frac{wt\mathscr{K}_{g_n}}{wt\mathscr{K}_{F_e}} = 0.0575 + 2.2788 \frac{I_{g_n}^w}{I_{F_e}^w} \qquad (15 - AP1)$$

Finally, Table 3-AP1 gives the ZAF-corrected mode Zn/Fe ratios.

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Figure 1-AP1. Plot of weight percent Zn/Fe Ratio (given by SQ-Tracor) versus net window Zn/Fe ratio.

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				F	ROM	PROG	RAM	SQ		
PARTICLE	window	k _{Fe}	k _{Zn}	<u>kga</u> kp.	(ZAF) _{Fe}	(ZAF) _{3n}	$\frac{(ZAF)_{g_{a}}}{(ZAF)_{g_{a}}}$	wt% _{Zn}	wt% _{Fe}	wt%r.
No	ratio <u>Iza</u> Ire									
1	0.0504	0.859	0.116	0.135	0.988	1.139	1.153	12.98	83.39	0.156
2	0.0610	0.853	0.115	0.135	0.978	1.140	1.166	13.16	83.22	0.158
3	0.0949	0.796	0.196	0.246	0.974	1.131	1.161	21.82	76.13	0.286
4	0.1022	0.773	0.208	0.269	0.976	1.128	1.156	22.39	71.95	0.311
5	0.1152	0.776	0.215	0.277	0.971	1.127	1.161	23.83	73.95	0.322
6	0.1368	0.735	0.258	0.351	0.964	1.119	1.161	28.52	69.82	0.408
7	0.1582	0.717	0.264	0.368	0.964	1.113	1.155	28.96	68.00	0.426
8	0.2577	0.529	0.304	0.564	0.980	1.072	1.094	30.11	48.76	0.618

Table 2-AP1 Quantitative-elemental EDS analysis of selected zinc ferrite particles in different magnetic fractions. Data to obtain parameters of equation 14

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Table 3-AP1	Uncorrected and ZAF-corrected mode Zn/	Fe ratios
for the mag	gnetic fractions with major proportions of zin	c ferrite.

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Current to the	Uncorrected mode Zn/Fe	ZAF-Corrected mode Zn/Fe
magnet	ratio	ratio
[mA]		(rounded)
40	0.13	0.34
80	0.123	0.34
130	0.185	0.48
180	0.214	0.55
211	0.214	0.55
250	0.210	0.54
300	0.20	0.51

APPENDIX 2 FOR MANUSCRIPT V Magnetic Susceptibilities by Foner Magnetometer

The Foner vibrating sample magnetometer [182] is a device of high precision $(\pm 0.5 \%$ relative accuracy claimed) which determines magnetization properties by monitoring the voltage induced in a set of stationary detection coils by the moving dipole field of a sample vibrating perpendicular between the coils in uniform field.

Samples of the Frantz fractions obtained at currents of 40 to 476 mA where investigated with the Foner magnetometer to obtain values of the high field magnetic susceptibility. The objective was to prove unequivocally that the obtained fractions in the Frantz were indeed different with respect to their magnetic susceptibility and that the Frantz fractions were not the result of mere mechanical splitting.

The measurements with the Foner magnetometer were performed by Prof. W.B. Muir from the Physics Department of McGill University [186]. Table 2-AP2 gives the results expressed as the magnetization of the sample relative to the magnetization of nickel.

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Table 1-AP2Magnetization relative to the magnetization of nickelfor the most significant Frantz fractions obtained from the cone-3Cyclosizer product of the low acid leach residue

Current to	Relative Magnetization
the magnet	w.r.t. Nickel
at which the	
Frantz Magnetic	M/MNi
was obtained	
[mA]	
40	0.31
80	0.11
130	0.03
180	0.019
211	0.0007
250	0.003
300	0.002
356	0.003
412	0.002

Table 1-AP2 clearly shows that the different fractions obtained in the Frantz separator have indeed different magnetic susceptibilities. The magnetic fractions obtained between 40 and 211 mA have a similar phase composition. All of them contain approximately 80% zinc ferrite and 20% hematite. Despite their similar phase composition, the table shows that the fraction obtained at 40 mA has a magnetization 0.31 times that of nickel, while the magnetization of the fraction obtained at 211 mA is only 0.001 times that of nickel.

APPENDIX 3 FOR MANUSCRIPT V Zinc ferrites in steelmaking dusts

Goldstein et al [81] have characterized steelmaking dusts from electric arc furnaces of several plants. They showed that the dusts produced in the making of plain-carbon steels contain zinc ferrite as one of the important phase constituents. It is interesting to note that they obtained some experimental evidence suggesting that the zinc ferrites in steelmaking dusts may also show compositional variation.

The data that illustrated this more clearly was also obtained by SEM-EDS analysis performed with the help of an image analyzer. Figure 1-AP3 is a reproduction of one of the figures reported by Goldstein et al [81]. It gives the percent of the particles with iron and/or zinc that fell in a particular range of the ratio $I_{zn}/(I_{zn} + I_{Fe})$; where Ii is the EDS peak intensity for a given element. A particle of pure iron or pure iron oxides will fall in the 0-5% histogram bar, particles of pure zinc or pure zinc oxide will fall in the 95-100% range and particles of pure stoichiometric zinc ferrite will fall in the range 30-35%.

Figure 1-AP3 is a clear illustration that the zinc ferrites in steelmaking dusts do not have a fixed stoichiometry but show a compositional variation. In fact this was the interpretation given by Goldstein et al [81]. Unfortunately this interpretation can be debated on the ground that a population of agglomerates containing variable proportions of stoichiometric zinc ferrite, iron oxides (or iron) and zinc oxide (or zinc) would give a similar histogram when analyzed by SEM-EDS. The samples analyzed by Goldstein et al did show the presence of phases like iron oxides and zinc oxides and also the presence of agglomerates. On the other hand, the magnetic

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separations performed by Goldstein et al were too crude to clearly show the relation of these compositional variations with magnetic susceptibility. In contrast, the results presented in Manuscript V do not suffer the same limitation. (see Discussion in Manuscript V).

In any case, the collected evidence establishes that zinc ferrites industrially produced as side products do not have a fixed stoichiometry but have a variable composition.



Figure 1-AP3 Histogram for the results of SEM-EDS analysis of particles composed by iron and/or zinc encountered in a carbon and low alloy steel dust.

SECTION IV

SUMMARY, DISCUSSION, CONCLUSIONS, AND ORIGINAL CONTRIBUTIONS

IV.1 SUMMARY AND DISCUSSION ON: SAMPLE PREPARATION FOR SEM AND STEM

The study of particulate samples by electron microscopy requires careful consideration of sample preparation. The two most common preparation methods for particles are the polished sample technique and the substrate sample technique. The fine-particle nature of the residues characterized in this thesis frustrated the use of polished specimen. Polished sample preparation produced samples with surface pores which were probably related to particle plucking during polishing; besides, the particles showed poor dispersion in the resin used for mounting the powders. Consequently the substrate sample preparation technique was adopted.

Simple sprinkling or air dispersion to prepare substrate samples proved to be also unacceptable due to sample agglomeration. Therefore dispersion in a liquid was used. Several dispersion techniques were tried. The one that gave the best dispersion and was adopted for most of the studies of samples with fine particles is described in Figure II.5.

Samples for electron microscopy studies are necessarily small. The sample preparation technique described in this thesis is similar to that used by Goldstein et al [81] for the characterization of steelmaking dusts. However they utilized only

one mixture with propanol. This forced them to use only 0.001 g of sample into 40 ml of propanol. In contrast, the method in this thesis allowed an initial sample for the first propanol mixture to be about 60 times greater than the one used by Goldstein et al. Taking a more representative small sample to prepare the second propanol mixture is easier since the solids in the first propanol are dispersed in a large volume of liquid. Therefore it is believed that the preparation method described in this thesis permits better samples of the powdered materials to be studied by electron microscopy.

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IV > SUMMARY OF FINDINGS

IV.2 SUMMARY AND DISCUSSION ON: CHARAC-TERIZATION AND SEPARATION OF THE COP-PER SMELTER DUST RESIDUE FROM THE KIDD CREEK PLANT

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The chemical composition of the sample was 6.0% Fe, 21.3%Zn, 26.2%Pb, 10.6%Cu, 1.8%As, 1.4%Sn and 0.6%Cd. The specific gravity of the sample was 4.5. Particle size analysis showed the sample to be 88 weight percent finer than 8 μ m.

Several phases were identified in the copper smelter dust by a combination of analytical techniques including thermodynamic predictions. The major (more than 10%) phases present are: PbSO₄, ZnO, and Cu₂O. The phases of medium abundance (between 1 to 10%) are: ZnOFe₂O₃, Cu₂OFe₂O₃, As₂O₃, and Fe₃O₄. The phases of minor abundance (less than 1%) are: ZnS, Cu₃As, and Cu₅FeS₄. It should be noted that zinc sulphate (ZnSO₄), zinc oxysulphate (ZnOZnSO₄), and copper sulphate (CuSO₄) are phases also predicted from thermodynamic analysis, however, they were not found in the residue since these phases are dissolved in the water used to slurry transport the dust. Several trace elements were identified by AA and/or XRF, but their phase relationships were not positively identified. (see Table 2 Manuscript II).

A common feature among all particles was their highly agglomerated and chemically heterogeneous state. The agglomeration is a result of the high temperatures prevailing in the operations where the dust originates. This particle heterogeneity limited the potential of physical separation methods.

Leaching with boiling H_2SO_4 (1.5M) for 20 minutes, dissolves nearly 30 %Cu,

50%Zn and 60%Cd with less than 10%Fe and 5%Pb recovery. Zinc dissolution appears to be a combination of rapid ZnO leaching and relatively slow ZnOFe₂O₃ leaching. Copper dissolution is related to Cu₂O leaching. The most important phases of zinc and copper that are refractory to sulphuric acid leaching are ZnOFe₂O₃ and Cu₂OFe₂O₃; consequently these phases tend to appear in the residue of the leach together with the PbSO₄ originally present in the dust.

The residue of the leaching was found to contain one magnetic fraction with a high magnetic susceptibility of 7-8 x 10^{-2} [S.I. units]. The characterization of this fraction indicated an intimate mixture of mainly zinc ferrite with some copper ferrite. Despite this fraction's high susceptibility, concentration of this phase by magnetic separation is limited. High gradient magnetic separation (HGMS) at a magnetic field of 0.69T and a flow rate of 9.7 cm/s recovered over 40 % Fe to the magnetic fraction and over 80 % Pb to the non-magnetics; zinc basically splits between the two fractions. Mixed particles of lead sulphate and zinc ferrite occured in both fractions. In the magnetics the particles were mainly zinc ferrites with some lead sulphate bonded. The particles in the non-magnetics show the opposite, they are mainly lead sulphate bonded with some zinc ferrite. This explains why the magnetic fraction still carries 18 %Pb corresponding to a lead-recovery of 13% in that product.

Despite the physical limits of the magnetic separation, this could be considered as a preconcentration technique. The non-magnetic product can be further processed as a lead concentrate or a bulk Pb/Zn concentrate. On the other hand, the magnetic product contains the bulk of the refractory oxides. The discharge, treatment or recycling of this product should be further evaluated.

EM observation of some ferrites in the copper smelter dust showed, from iron-X-ray maps, more concentration of iron towards the centre of the particle. Based on this a speculative mechanism of ferrite formation was proposed. Solid iron oxides act as reaction centres where zinc (vapor) and copper {liquid} oxidize and are fixed according to:

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$$\langle Fe_2O_3 \rangle + (Zn) + 0.5(O_2) = \langle ZnOFe_2O_3 \rangle \qquad \Delta G^{\bullet}_{1473} = -169.87kJ$$

 $\langle Fe_2O_3 \rangle + 2\{Cu\} + 0.5(O_2) = \langle Cu_2OFe_2O_3 \rangle \qquad \Delta G^{\bullet}_{1473} = -69.04kJ$

This mechanism of ferrite formation agrees with the proposed by Yargin et al. (105). The higher (negative) free energy favours sinc ferrite formation which agrees with the predominance of this compound over copper ferrite.

IV.3 SUMMARY AND DISCUSSION ON THE CHARAC-TERIZATION AND SEPARATION OF METALLUR-GICAL RESIDUES FROM THE KIDD CREEK ZINC PROCESSING PLANT

IV.3.1 The Jarosite Residue

The chemical composition of the jarosite residue determined was 7.2%Zn; 34.8%Fe and 1.6%Pb. The specific gravity was 2.7. Particle size analysis determined the residue to be 80% finer than $\approx 12 \ \mu m$. Characterization of the residue showed that the most important phases present in this residue were sodium jarosite, NaFe₃(SO₄)₂(OH)₆ and zinc ferrite, ZnOFe₂O₃.

The magnetic profile of the jarosite residue showed the presence of two distinct magnetic fractions with magnetic susceptibilities of 7.3×10^{-3} [S.I. units] and 1.0×10^{-3} . The characterization of the two magnetic species showed that the one with the higher magnetic susceptibility was mainly zinc ferrite, the other magnetic product was sodium jarosite.

The SEM study revealed that the two phases are not intergrown. This explained the high degree of phase separability obtained in the Frantz magnetic separator. In spite of that, the industrial magnetic separation of zinc ferrite from sodium jarosite will be limited because the ratio of their magnetic susceptibility is only $\approx 7.5:1$ (106).

As in the case of the Cottrell dust, high gradient magnetic separation tests were performed for the jarosite residue. In general, it was found that as the magnetic field increased, the zinc recovery to the magnetic fraction increased, but the zinc grade decreased. This reflects the increased recovery of the lesser magnetic phase, jarosite, at increasing magnetic field strengths. Separation was somewhat enhanced by incorporating roughing and cleaning magnetic stages, the results showed a zinc recovery of 39 % into the cleaner magnetic product at a grade of 15 % Zn.

Besides the sodium jarosite and the zinc ferrite, other phases were also identified in the jarosite residue: as a medium abundant phase (from 1 to 10%) SiO₂; and in small proportions (less than 1%): feldspars, ZnS, FeS, Cu₂FeSnS₄, Cu(Fe,Sn)₂S_{3.9} and Cu-Zn-Fe-Sn silicates.

IV.3.2 Hot acid leach residue

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The sample was a grey-black residue of specific gravity 3.1. The chemical composition was: Zn 9.80%; Fe 11.72%; Pb 7.94%; Cu 0.60%. Size analysis by cyclosizer showed the sample was over 80% finer than 10 μ m.

The characterization of the HAL residue showed that the following phases were present: of major abundance (more than 10%): $ZnOFe_2O_3$, Fe_2O_3 , and SiO_2 ; of medium abundance (between 1 to 10%): SnO_2 , $PbSO_4$, and or $PbOPbSO_4$, $PbFe_6(SO_4)(OH)_{12}$, $PbCS_3$, ZnS, $H_2Ca_2Zn(AsO_4)_2(OH)_2$ and CuS_2Sb ; and of minor abundance (less than 1%): MnO_2 , FeS, Cu_3FeS_4 , Fe_9S_8 , S, Cu_2FeSnS_4 , and Cu-Zn-Fe-Sn silicates.

The magnetic profile of the HAL residue showed one major magnetic species with a magnetic susceptibility of $\approx 4.0 \times 10^{-3}$ [S.I. units]. Characterization showed that zinc ferrite was the constituent of the major magnetic fraction. Lead jarosite, PbFe₆(SO₄)(OH)₁₂, was found to be a minor magnetic phase.

The ferrites present in the HAL residue (and in the jarosite residue) were significantly less magnetic than those ferrites in the Cottrell dust. This is due to lower amounts of incorporated copper ferrite in the zinc ferrites in the HAL and jarosite residues.
As in the case of the Cottrell dust and jarosite residues, high gradient magnetic separation (HGMS) tests were performed with the HAL residue. Separation at a magnetic field of 1.8T and a flow rate of 9.7 cm/s gave a sinc recovery to the magnetic fraction approaching 30% with a grade of 20-22% Zn, corresponding to a 75-80% sinc ferrite. Lead in the magnetic fraction is less than 2%. Over 98% of the lead goes to the non-magnetic fraction. For this residue, therefore, HGMS appears to be an attractive option since it gives a clean, almost lead-free zinc ferrite concentrate.

The proposal that sinc ferrites form by reaction on an iron oxide nucleus would imply that the zinc in the outer reaction layers is easier to leach. This mechanism of formation and dissolution would disclose zinc ferrite with variable Zn/Fe ratios. EDS analysis of some ferrite particles in the hot-acid-leach residue seemed to support the proposal of zinc ferrites with variable Zn/Fe ratios, the results also suggested that variable composition of the zinc ferrites was related to variable magnetic susceptibility.

IV.4 SUMMARY AND DISCUSSION OF THE FIND-INGS ON: ZINC FERRITES IN THE LOW-ACID LEACH RESIDUE OF CEZ

The SEM-EDS study performed with the low-acid leach residue of CEZ (Manuscript V) was designed to test the hypothesis of a variable Zn/Fe ratio in the zinc ferrites produced from roasting of zinc sulphide concentrates.

The evidence of a variable zinc ferrite composition was obtained from the Frantz magnetic fractions of a coarse ($\approx 19 \ \mu$ m) near monosized fraction of the low-acid leach residue. Zinc ferrite was the major phase present in all the Frantz fractions obtained at the following magnetic fields: 0.03T, 0.06T, 0.11T, 0.18T, 0.25T, 0.29T, 0.34T and 0.41T. Despite the similar phase composition of these fractions their values of magnetic susceptibility changed markedly. Approximately 100 particles of each fraction were analyzed by SEM-EDS with the help of an image analyzer.

The results showed that the modal Zn/Fe ratio of the zinc ferrite particles in the different magnetic fractions was not constant but changed, increasing in the fractions obtained at higher magnetic fields. The variation in Zn/Fe ratio was not due to a mixture of stoichiometric zinc ferrite and magnetite. Therefore the zinc ferrites produced in the roasting of zinc sulphide concentrates have variable composition which is related to their magnetic susceptibility. The higher the Zn/Feratio the lower their magnetic susceptibility. The results agree with the reported magnetic behavior of synthetic zinc ferrites of variable composition [180, 181].

There is a possibility of recovering zinc ferrites magnetically from the residues to recycle them to the leaching plant. However, if the magnetic separation is done at relatively low magnetic fields, then the recovered zinc ferrites will have lower Zn/Fe ratio. The recovery of these ferrites will be less attractive considering that the main objective is to increase the recovery of sinc.

It is believed that the variable Zn/Fe ratio also influences leachability. The presence of crystal-like ferrites with lower Zn/Fe ratios in the HAL residue, suggests that the ferrites with lower Zn/Fe ratio are more refractory to leach. If this is true then the continuous magnetic recovery and recycle could result in a build-up in the leaching circuit of ferrites with low Zn/Fe ratio. This could be avoided by performing two magnetic separations one of a high magnetic field and a second at a low magnetic field. The second step would remove the ferrites with low Zn/Feratios. The ferrites with high Zn/Fe ratios then would be recycled to the leaching plant (i.e. HAL or pressure leaching) and the ferrites with low Zn/Fe ratios could be discharged or processed with more intensive pyrometallurgical methods (e.g. plasma furnace or cyclone furnace).

The supposition that zinc ferrite with variable composition will have different dissolution behavior in sulphuric acid is understandable, other solid solution systems show such differential behavior [120]. However, the suggestion that zinc ferrites with low Zn/Fe ratios are harder to leach could be debatable. It is necessary to experimentally confirm the leachability of zinc ferrites as a function of their Zn/Fe ratio. As described, the Frantz magnetic separator can be used to separate fractions of zinc ferrites with variable composition. Unfortunately, application of the Frantz to obtain adequate amounts of samples for leaching tests is time consuming. This is due to the fact that the perfection of the magnetic separation in the Frantz is achieved by using very low feeding rates.

A possible approach is to synthetically produce several samples of zinc ferrites with different and discrete values of ratio Zn/Fe. The method of production could be that used by Stuijts et al [182] and successfully applied by others [180, 181]. The samples thus produced would give insight into the behaviour in leaching of sinc ferrites with different Zn/Fe ratios. However, a problem which may have to

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be considered is that the mechanism of formation of the ferrites in those synthetic samples could be different from that of the ferrites produced on roasting and this may also play a role in the leaching behaviour.

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GENERAL CONCLUSIONS

1.-The following residues have been characterized:

-The copper smelter dust from the Kidd Creek plant.

-The jarosite and the hot-acid-leach residues from the zinc Kidd Creek plant.

-The low acid leach residue of the Canadian Electrolytic Zinc plant.

The three first residues have been extensively characterized, whereas the fourth residue was used to focus on the characterization of the zinc ferrite component.

- 2.-Several phases were identified in the residues; zinc ferrite was found present in all of them. This phase is important because it is correlated with zinc losses in the zinc extraction process and as it is a refractory phase. Zinc ferrite is present even in the residue of the leaching performed with hot sulphuric acid.
- 3.-The results with the copper smelter dust showed that a combined treatment of hot-sulphuric acid leaching and magnetic concentration can separate some of the elements present in the dust. The leaching step dissolved nearly 30 %Cu, 50 %Zn and 60 %Cd with less than 10 %Fe and 5 %Pb. The magnetic fraction recovered 40 %Fe and the non-magnetic fraction 80 %Pb. However zinc, (as ferrite) essentially splits between the two magnetic products. This is partly due to agglomeration and partly due to ferrites apparently having a range in magnetic susceptibility.
- 4.-In the case of the jarosite residue, separation of zinc ferrite from sodium jarosite by magnetic means is limited because the difference in magnetic

susceptibility between the two phases is not enough to achieve a clean separation.

- 5.-For the hot-acid-leach residue, concentration of sinc ferrite in a magnetic product is feasible. Results showed up to 75 wt %. of the ferrite was recovered to the magnetic product with over 98% of the lead being rejected to the non-magnetic product.
- 6.-Evidence is presented which strongly indicates that the zinc ferrite in these residues does not have a fixed composition (e.g. $ZnOFe_2O_3$) but exhibits a compositional variation (e.g. $Zn_2Fe_{3-2}O_4$ with 0.7<x<1). This causes a variation in the magnetic susceptibility of the ferrite. The compositional variation of the ferrite must be considered if magnetic recovery and recycling of the ferrite is planned.

ORIGINAL CONTRIBUTIONS

- 1.-Zinc ferrites from several sources have been studied by a combination of techniques which included magnetic characterization, X-ray diffraction and electron microscopy. A contribution has been made in demonstrating that zinc ferrites produced in the roasting of zinc sulphide concentrates exhibit a variable Zn/Fe ratio from ≈ 0.35 to ≈ 0.55 . This indicates a composition variation of the type $Zn_zFe_{3-z}O_4$ where 0.7 < x < 1. The variable composition of the ferrites corresponds to the measured variation in magnetic susceptibility; the lower the Zn/Fe ratio value the higher the magnetic susceptibility. The fact that industrially produced zinc ferrites have variable magnetic susceptibility helps in understanding the limitations of magnetic methods of separating zinc ferrites.
- 2.-The complex nature of the fine-particle residues impedes the completeness of their characterization. A contribution has been made to the sample preparation technique for X-ray and electron beam studies for characterization of these residues. The sample preparation technique makes extensive use of fractionation exploiting the the different properties of the components viz. particle size, leachability and magnetic susceptibility. These fractions are less complex than the original residues making characterization easier. For example, the precise magnetic fractionation of leach residues using the Frantz isodynamic magnetic separator proved to be a key technique in disclosing the variability in composition of the zinc ferrites produced in the roasting of zinc sulphide concentrates.

SUGGESTIONS FOR FURTHER RESEARCH

- 1.-Determination of the sulphuric acid leachability of zinc ferrites as a function of their Zn/Fe ratio to asses the behaviour of recycled ferrites.
- 2.-Use of high resolution TEM for lattice imaging, EDS or EELS and convergent beam electron diffraction to determine the lattice parameters as a function of Zn/Fe ratio of the zinc ferrites produced in the roasting of zinc sulphide concentrates.
- 3.-If Mössbauer spectrometry is capable of discriminating between zinc ferrites of close composition, then this technique could be used to further substantiate the compositional variation observed by the techniques used in this thesis.

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