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FACTORS AFFECTING BEHAVIOUR OF MINOR ELEMENTS IN DORE METAL - SODA SLAG PARTITIONING

By Tatiana Luganova-Chnyrenkova

A Thesis Submitted to the Faculty of Graduate Studies and Recearch in Partial Fulfillment of the Requirements for the Degree of Masters of Engineering

> Department of Mining and Metallurgical Engineering McGill University Montreal July, 1994



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ISBN 0-315-99973-X



To my dear parents, husband and son

ABSTRACT

A series of experiments determined the influence of oxygen partial pressure and SiO₂ content in soda slag on the distribution of metals between soda slag and dore metal. Oxygen partial pressure ranged from 10^{-3} to one atmosphere and the SiO₂ content from 0 to 10 wt%.

At Canadian Copper Refiners (CCR), copper tankhouse slimes, bearing precious metal, are treated in batches in a Top Blowing Rotary Converter (TBRC). The treatment is carried out in three stages - smelting, lead converting and refining. In the final stage of the treatment, sodium carbonate is added to the TBRC vessel and is followed by oxygen blowing. The purpose of the soda refining step is to eliminate tellurium and some copper from the melt. Minor elements, including the precious metals, partition between the dore metal and the soda slag. The main purpose of this research was to determine the process parameters which influence this distribution, and the nature and forms of the precious metals in the metal and in the slag phases.

From the results of the experiments it was found that:

- (a) Increasing oxygen partial pressure from 10⁻⁸ to 1 atm does not influence gold, palladium and platinum removal from dore metal, but leads to the practically complete removal of Te (down to 4.8 ppm), Rh (down to 2.7 ppm), Pb (down to 6.0 ppm) and quite good removal of Se (down to 0.0112 wt%) and Cu (down to 0.42 wt%) from the dore metal.
- (b) Silica content of the soda slag does not influence gold, palladium and platinum chemical losses with soda slag. However it was found that increasing silica in slag leads to an increase of mechanical loss of precious metals because of the increase in slag viscosity.
- (c) Increase in silica content of slag increased lead and copper removal from dore metal, and decreased the removal of rhodium, selenium and tellurium, especially at low oxygen potential.
- (d) It was concluded that most of precious metals leave dore metal in the form of mechanical losses, but silver and rhodium were found in slags as intermetallic phases with the other components. Rhodium is also lost in the form of the volatile oxide RhO₂.

RESUME

Des expériences ont determine l'influence de la pression partielle d'oxygène et de la teneur en SiO₂ dans la scorie sodique sur la répartition des métaux entre la scorie sodique et le métal doré. La pression partielle d'oxygène varie entre 10^{-8} et 1 atm et la teneur en SiO₂ de 0 à 10% en poids.

Une innovation récente est utilisée à Canadian Copper Refiners (CCR) pour fondre des boues anodiques riches en métaux précieux dans un convertisseur rotatif à soufflage par le haut (Top Blowing Rotary Converter TBRC). Le TBRC est opéré en mode discontinu à CCR. Lors de l'étape finale d'affinage de la charge, du carbonate de sodium est ajouté dans la cuve du TBRC suivi d'un soufflage d'oxygène. Le but de cette étape d'affinage à la soude est d'élimine le tellure ainsi qu''une partie du cuivre. En plus, des éléments mineurs, essentiellement des métaux précieux, se répartissent entre le métal doré et la scorie sodique. Le but principal de la recherche a été de distinguer quels paramètres du procédé influencent cette distribution ainsi que la nature et les formes des métaux précieux dans le métal et dans la scorie sodique.

A partir des résultats des expériences, il a été trouvé que:

- (a) L'augmentation de la pression partielle d'oxygène de 10⁻⁸ à 1 atm n'influence pas le retrait de l'or, du palladium et du platine du métal doré mais entraine une élimination pratiquement totale de Te (jusqu'à 4.8 ppm), Rh (jusqu'à 2.7 ppm), Pb (jusqu'à 6.00 ppm) et une assez bonne élimination de Se (jusqu'à 0.0112% en poids) et Cu (jusqu'à 0.42% en poids) du métal doré.
- (b) La teneur en silice du scorie sodique n'influence pas les pertes chimiques d'or, de palladium et de platine avec la scorie. Cependant, il a été trouvé qu'une hausse en silice entraine une augmentation des pertes mécaniques des métaux précieux à cause d'une augmentation de la viscosité de la scorie.

- (c) Une hausse en silice dans la scorie augmente le retrait du plomb et du cuivre du métal doré et diminue le retrait du rhodium, du selenium et du tellure, particulièrement à faible potentiel d'oxygène.
- (d) Il a été conclu que la plupart des métaux précieux quitte le métal doré sous forme de pertes mécaniques, mais l'argent et le rhodium ont été trouvés dans les scories sous forme de phases intermétalliques avec d'autres composants. Le rhodium est aussi perdu sous la forme d'oxide volatile RhO₂.

ACKNOWLEDGEMENTS

I was fortunate to have the support and help of many people during my graduate studies at McGill University. I would like to express my gratitude to all the members of the McGill Metallurgical Department.

I would like to thank specially professor Ralph Harris, my thesis supervisor, for his advice, generosity and encouragement throughout the research work.

I want to further thank my fellow graduate students Masashi Ikezawa, John Roumeliotis, Peter Hancock, Rui-Qing Li and Michel Laurin for their friendship, great working environment, help and support in solving problems and for the interesting feedback. Also I would like to express my sincere thanks to professor W. Williams and H. Mulasimoglu for their friendship and support in all the aspects of my work.

Finances and most of the materials for my project were provided by the CCR, Noranda Minerals Inc. Needless to say that none of this work would be done without it. Special thanks to Ernest Mast, who helped to arranged and put this project together, for his help with this work during two years.

I appreciate the time taken by the personnel of the Noranda Technology Centre for the project follow up and for the sample assay. More specifically thanks to Dr. Dan Poggi for giving me a chance to do experimental work on their equipment. Thanks to Line Mongeon for the great help with the SEM analysis.

It was a pleasure to meet Dr. J. Dutrizac and have a discussion with him which helped to understand some important details in my work. Table of Content

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LIST OF SYMBOLS

P _{o2}	Partial pressure of oxygen in a gas phase, atm
Т	Temperature, OC
P _{co2}	Partial pressure of CO_2 in a gas phase, atm
- log a _{N-20}	The defined basicity of slag
L _{Me}	Distribution coefficient between dore metal and soda slag
X _{Me dure metal}	Mass % of impurity metal in dore metal
\mathbf{Y}_{Me} and a line	Mass % of impurity metal in soda slag.
a _{pb}	Activity of lead in dore metal
B _{Cu}	Activity of copper in dore metal
a _{Ka}	Activity of rhodium in dore metal
a _{CuO_{0.5}}	Activity of copper oxide in slag
x.	Solubility of oxygen in silver
YA	Activity coefficient of gold in silver
Υ*rs	Activity coefficient of lead in silver
∆G	Gibbs energy of reaction.



CHAPTER 1. INTRODUCTION

1.1 Introduction

Precious metals such as silver, gold and the platinum group metals have many unique and useful properties, for example, the ability to form workable alloys with each other and with additional elements. The catalytic properties of the platinum group metals are outstanding and the beneficial characteristics of Ag, Au and Pd as electrical contacts are generally recognized (1, 2, 3, 4, 5, 6). All these properties are extensively exploited in commercial practice, Table 1.1.

	Precious metals demand by application: Western World (%), 1988					
	Pt	Pd	Rh	Ir	Ru	Au
Jewelry	33	5	-	-	-	80
Autocatalyst	32	6	73	-	-	-
Investment	17		-	-	-	7
Chemical	5] -	10	36	38	-
Electrical	5	51	4	-	-	-
Glass	4	-	6	i -	-	-
Others	3	8	7	29	11	3
Petroleum	1	-	-	12	-	-
Dental	-	30	-	-	-	3
Electronics	-	-	-	-	51	7
Catalyst	-	-	- 1	9	-	} _
Crucibles	-	-	-	14	-	-

Table 1.1. Applications of precious metals.

Gold, silver and platinum often occur as a native metals. Before 1914, most of the native precious metals came from Russia and South America. Today, major sources of native metals include Alaska, Colombia, Russia and South Africa (the average amount of newly mined native gold is now around 1000 metric tonnes per annum), but the contribution of native metals to overall output is only a half of world production, Table 1.2.

Chapter 1. Introduction

	Precious metals supply for 1988, (tonnes)				
	Pt	Pd	Au	Ag	
South Africa Canada	80.2 4.5	34,4 5,3	621 128	1216	
Others: Other Africa USA Latin America Asia (India) Europe Australia Total	- - - 3.0	- - - - 8.4	67 205 226 81 19 152	- 4054.4 (822.4) - 1123.2	
USSR (Sales) Total	13.7 101.4	55.1 103.1	258 -	-	

Table 1.2. Platinum, palladium and gold world output for 1988 (1).

The other half of world production of precious metals is derived from the copper-nickel sulphide ores of Canada, South Africa and Russia. These ores contain of the order of only grams of these metals per tonne. Thus full treatment of complex ores to recover precious metals has become a world wide focus. Each company is trying to find its own, better way of treating the ores to recover as much of the precious metals as possible and at the lowest cost.

1.2 Recovery and refining of precious metals

The variety of processes used in the recovery and refining of precious metals may be classified into two categories. These process categories are based on the differences in the raw materials sources:

- a) from the concentrates of mined platinum bearing copper-nickel sulphide ores;
- b) from secondary material sources such as recycled industrial products.

Several different processes for recovery and refining of these secondary raw materials sources have been practised industrially. The method chosen depends on the physical form of the source, its precious metal content and the nature of other elements present. Generally speaking, the first step is to make a solution by acid leaching. Precious metals are recovered by electrowinning, ion-exchange or group separation precipitation (GSP)^{*}.

1.2.1 Recovery and refining of platinum group metals

Precious metals become concentrated in the sulphide matte which is produced during the smelting of the ore concentrates. In the Orford process (7), sodium sulphide is added to the matte, thereby forming two separate copper and nickel matte phases. The metals are recovered from these mattes by a converting process which yields a crude metal product suitable for electrorefining. The anode slimes obtained by electrorefining the crude nickel contains the main portion of the platinum group metals.

The slime concentrates are air roasted. Copper and nickel are leached out with sulphuric acid, to yield PGM-enriched residues from which the platinum group metals are further concentrated by melting them with charcoal and litharge to form a lead button. The resulting lead alloy is nitric acid leached. The acid insoluble residue becomes a raw material for further refining. The pressurized carbonyl process practised by INCO Canada strips nickel as a gaseous nickel carbonyl, and leaves a residue that contains the platinum group metals (8, 9).

INCO Canada have also developed a new pressurized carbonyl process for the crude nickel metal and now operates a solvent extraction process for precious metals recovery refining. For this process the raw materials are the copper electrorefining anode slimes (10, 11)

The Matthey Rustenburg Refinery has also developed a solvent extraction process which uses oxime/amine extractants. This technology is based on the "straight chain process" (12, 13).

GSP is a method based on separate precipitation of a group of compounds containing the same precious metal.

1.2.2. Recovery and refining of gold and silver

As already mentioned, much of the world gold and silver production derived from the base metal sulphide concentrates such as copper, lead and zinc, including their arsenides, tellurides and antimonides. The gold and silver become concentrated in the electrolytic refining anode slimes. Gold and silver silicious ores have been used as a slag forming fluxing agents in the pyrometallurgical processes for the production of copper and lead, whereby the gold and silver later become concentrated in the electrolytic slimes (14, 15, 16).

The following is the general process outline for gold and silver recovery from copper anode slimes (1).

- 1. The anode slimes obtained from electro-refining crude copper contain all the precious metals along with other elements such as Se, Te, Pb, Cu, As, Bi, Sb, Ba, Si and insoluble sulphide compounds.
- 2. Slime pretreatment eliminates much of the base metal content. Copper is removed by leaching with sulphuric acid and agitated air; sulphides, e.g. lead sulphide, are removed by flotation.
- 3. The slime is then melted in a small reverberatory furnace where selenium is volatilised as selenium dioxide, which is recovered in an absorption tower. Litharge, fluxes and carbonaceous material are added for reductive melting to produce a lead alloy containing gold and silver.
- 4. The lead alloy is transferred to a rotary furnace, where it is melted with soda ash, sodium nitride and oxidized by air-lancing. This oxidation operation transforms lead and other base metals into oxide slags and silver-gold alloy remains at the bottom of the furnace. The silver-gold alloy is cast into anodes, which are electrorefined.

1.3 Slime treatment process at Canadian Copper Refinery

As already mentioned, the recovery of precious metals is widely practiced. But each producer struggles to develop the cheapest process for each particular type of ore. One such company is Canadian Copper Refinery (CCR), Noranda, the largest producer of refined silver in Canada (approximately 1000 tonnes per year), and one of the world largest selenium producers (about 400 tonnes per year).

CCR four years ago started to use a new, unique process for the slime treatment: the TBRC (Top Blown Rotary Converter) process. Previously, CCR used a conventional flowsheet for slimes treatment, which included three roasters for selenium removal and a Dore furnace to produce silver anodes. Unfortunately, the conventional flowsheet contained four sources of selenium emission to the atmosphere (the roasters and the Dore furnace), requiring four independent scrubber systems which are costly to operate under the stringent requirements of the Montreal Urban Community, where CCR is located.

The main purpose of the new TBRC smelting process was to reduce the number of possible sources of emission through the use of a rotating vessel, oxy-fuel burners and tonnage oxygen. This kind of process has long been established in the ferrous and many sectors of nonferrous metallurgy, but is only now being applied to precious metals processing. A new slimes smelting process was envisaged, wherein the tumbling action of the anode slimes in a rotating furnace, intensive heating from an oxy-fuel burner would accelerate elemental selenium separation by volatilization prior to smelting and wherein the impurity elements, principally selenium and lead, would be separated from the molten phase containing the precious metals by intensive blowing with commercially pure oxygen. The functions of the three roasters and the Dore furnace were thus combined into a single intensive smelting unit, the Top Blown Rotary Converter, TBRC.

1.4 Treatment of de-copperised slimes in TBRC

De-copperised slimes are a complex mixture of elements and compounds which are not electrolytically oxidized in the anodic dissolution process, electrorefining, or oxygen pressure leaching (17).

The compounds remaining after de-copperizing include elemental silver, gold, platinum group metals, elemental selenium, Ag_2Se and AuAgTe. Compounds such as PbSO₄ and NiO which are formed during anodic dissolution also report to the de-copperised slimes. CCR slimes also contain a significant amount of BaSO₄ originating from the barite mold wash used in copper anode casting.

Typical assays of the de-copperized CCR slimes as well as foreign slimes treated at CCR are shown in Table 1.3.

The Top Blown Rotary Converter was chosen for slime treatment at CCR, because it combines high roasting and smelting rates with high oxygen efficiency. Advantages of the TBRC include (17):

- (a) High smelting rates: the rotating action of the vessel continuously exposes fresh surfaces to the flame allowing uniform heating of the charge, good selenium elimination prior to melting, and fast melting of the charge.
- (b) Ideal shape for blowing: the vessel shape presents a deep bath for blowing over the wide range of fill volumes.
- (c) Good access to the bath: the large mouth of the vessel combined with the ability to tilt the furnace gives the operators good access for slag removal.
- (d) The rotation of the TBRC prevents formation of a slag line which would rapidly erode the refractory lining of the vessel under intense blowing operations.

Because of these advantages the application of the TBRC in anode slime smelting is gaining increasing prominence (17).

Element	CCR De-Copperized Slimes, wt %		Foreign Slimes, wt % (kg/t)
	Average	Range	Range
Cu	0.8	0.3-1.0	0.4-2.5
Se	16	12-20	0.2-58
Te	0.5	0.3-0.7	0.02-0.4
Pb	15.7	12-28	3-50
As	0.5	-	0.05-0.2
Sb	0.4	-	0.1-3.2
Bi	0.7	-	0.1-0.5
Ba	4.0	-	-
Sn	-	-	0.2-0.8
Ag	32.5	24.5-38.0	7.5-32.5
Au (kg/t)	0.98	0.84-1.12	(0.25-2.2)

Table 1.3.Analysis of slimes.

The TBRC process consists of three main steps:

- (a) Smelting
- (b) Lead Converting
- (c) Refining

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The purpose of the smelting step is to smelt slimes, charge reverts and scrap and to eliminate easily removed impurities with a silica flux.

The furnace atmosphere during smelting is slightly oxidizing, because burners are operating in stoichiometric ratio, and some oxygen is released as a result of decomposition of compounds, such as $PbSO_4$, Ag_2O and Ag_2SO_4 . In general, all the refractory oxides and sulphates present in the feed such as Al_2O_3 , $BaSO_4$ and SiO_2 report to the slag. Also, a large quantity of $PbSO_4$ reports to the slag according to the reaction:

$$PbSO_4 + HEAT = PbO_{slow} + SO_2 + 0.5O_2$$
 (Eq. 1.1)

The refractory oxides, the high SiO_2 content, and the large percentage of unreacted sulphate material tend to make a "sticky" slag with a high liquidus temperature, compared to the slags without SiO_2 or with low SiO_2 content. This contributes to a high precious metal loss (as much as 5.5 wt % Ag) in this initial slag (18).

Due to the high partial pressures of SO_2 above the melt, the remaining Pb in the system exists as PbS in solution with a silver selenide matte (18).

The lead converting part of the process eliminates lead from the melt. The slags formed in lead converting are relatively simple: they are composed mainly of PbO and the SiO_2 that is added as flux in order to reduce lead vapour pressures (lead reporting to scrubber) and to render slag less chemically aggressive towards the TBRC lining. The basic lead converting reactions are:

$$PbS_{(matrix)} + O_{2(1)} = PbO + SO_2$$
 (Eq.1.2)

$$PbO + SiO_2 = (PbO * SiO_2)_{(alag)}$$
(Eq.1.3)

After most of the lead has been removed as a lead silicate slag and the slag has been skimmed, the bath is essentially silver selenide matte (Ag₂Se). The oxygen lance continues to blow and selenium is volatilized from the bath according to the reaction:

$$Ag_{2}Se + O_{2} = 2Ag + SeO_{2}$$
 (Eq. 1.4)

The refining step is a soda ash (Na_2CO_3) treatment to eliminate the remaining minor elements, especially Cu and Te. Oxygen injection and soda ash result in copper being slagged as Cu₂O while Te most likely reacts with the sodium carbonate to form sodium tellurite, according to the following equation (18):

$$2Na_{2}CO_{3} + 2Te + 2O_{2} = 2Na_{2}TeO_{3} + CO_{2}$$
(Eq. 1.5)

Interaction between tellurides present in the system and sodium carbonate does not produce tellurium trioxide (19). Matveeva and Soshnikova found that the first oxidation product was sodium tellurite, which is water soluble, but if the mixture of tellurides contained a copper compound the yield of water-soluble tellurium was lowered. This observation was attributed to the formation of insoluble sodium copper tellurites and tellurates. Also, extra Na₂O was left in the system helping to fluidize the slag by a sodium oxide-silica chemical interaction, since there is always some silica remaining in the system after the previous steps.

Typical composition of slags for each step of the TBRC process is shown in Table 1.4.

Chapter I. Introduction

Compound	Stag composition, %			
	Smelting	Lead Converting	Refining	
Pb	22.6	8.6	4.9	
SiO ₂	17.6	37.5	9.3	
BaSO,	4.2	3.5	-	
SO₄	5.7	-	-	
Al ₂ O ₃	1.3	0.34	-	
Te	0.3	0.6	9.4	
Se	2.1	2.9	-	
Cu	2.0	3.3	11.8	
Ag	5.5	9.9	11.3	

Table 1.4. Typical slag composition for three steps of the TBRC process (18).

During the refining step of the TBRC process, significant loss of precious metals with soda slag occurs. The soda slag is not easily cleaned of precious metals by milling due to its high Na content, and because of this, this low tonnage material is stored separately and recycled to the TBRC during the initial phases of subsequent cycles. This means that a significant amount of Te and noble metals are returned to the furnace. Chemical analysis of soda slags can show up to 12 % Ag, 3700 ppm Au and 1000 ppm Rh. Because of these high values of precious metals, it is of great commercial interest to find out in what form the precious metals report to the soda slag so as to discover a way to reduce the losses.

1.5 Objectives of the present work

Behaviour of minor elements in the dore metal - soda slag - gas phase system is influenced by a number of factors. The literature review will show that the most important factors for this type of system are the P_{o_2} of the gas phase, the chemistry of soda slag and the chemistry of the metallic phase.

The objectives of the present work were:

(i) To find out the influence of P_{o_2} on the system by performing equilibrium partition experiments under different oxygen potentials of the gas phase:

- F*A*C*T modelling to predict the behaviour of the system

- Experimental work to show the influence of the P_{O_2} on the distribution coefficients of minor elements between dore metal and soda slag.

- (ii) To examine the influence of the SiO₂ content of the soda slag on the distribution coefficients of minor elements between dore metal and soda slag.
- (iii) To see what changes have to be introduced to the TBRC process to reduce precious metals losses.

2.1 Introduction

Study of the impurity behaviour, from the point of view of metal loss and the compounds containing precious metals which form within the liquid slag during soda ash refining of dore metal is an important matter, because a reduction in metal loss with a slags can be achieved much more effectively with such knowledge. This type of knowledge will also help prognosis the metals' behaviour involved when there are changes in refining technology.

Some work has been done in order to solve this problem (20,21,22) for different types of processes: flash smelting, bath smelting, slag-cleaning smelting. However, the published results did not give a clear answer to the question of how noble metals loss occurs, especially in dore metal refining

Riabco et al. (23) developed an empirical method of calculation based on experimental results for slag-cleaning and ore-smelting furnaces. These calculations distinguished amounts of noble metals lost chemically and mechanically. However, the report did not identify phases containing precious metals in slag and gas phase. Samoilov et al. (24) found in their work on nickel concentrates treated in an industrial flash smelter that all the noble metals, including Ag and Os, had 90% recovery. Some was present in the slags and up to 0.5% Ag and Os was found in elemental sulphur produced from the outgoing gases in the sulphur plant. In a work (24a) on the behaviour of platinum group metals in production of anode Ni by oxidizing-vacuum technology it was also mentioned that the average composition of dust during all the steps of the process had the same chemical composition as the anode Ni (Ni-81.17-67.82%, Cu 5.11-8.10% based) excluding silver, which was 10 times higher than in the anode Ni.

From private communication it was learned that some study was done at Noranda Technology Centre (NTC) on precious metal loss to smelting and converting slags in the TBRC. In general, results indicated two principal features of slag chemistry which influenced silver loss to slag: (i) the slag Pb:SiO₂ ratio and (ii) the amount of sulphate sulphur in slag. The general comment was that precious metal content in slag increased with increasing slag viscosity. The experience of all these researchers was very interesting, but nothing was found in a literature

about dore-metal - soda slag interaction and also about the behaviour of the impurities during the TBRC process.

As was presented in the Introduction, the TBRC dore metal production is unique and does not have any analogies elsewhere a world industry. Perhaps because of this fact any research results about the behaviour of impurities (Au, Cu, Pb, Se, Te, Pd, Pt) during the TBRC process have not been published.

In order to understand in what forms and chemical compounds impurities can be present in dore metal and soda slag it is necessary to start from the chemistry of anode slimes - the starting material for dore metal production.

2.2 Anode slimes

The mineralogical characterization of the anode slimes treated at CCR was carried out at CANMET Mineral Science Laboratories (25, 26). There was found that raw anode slimes "consist principally of various Ag-Cu oxides, PbSO₄, BaSO₄, CuSO₄*5H₂O and an oxidate matrix phase which agglomerates the slime particles ". The "oxidate" matrix phase consisted of major amounts of Ag, Sb, Pb, SO₄ and Se together with minor quantities of Si, Te, As, Bi, Au, Pt and Pd. Copper occurs principally in the selenide phases, but a minor amount of this element is also present in the copper sulphate. Gold, platinum and palladium sometimes are detected in the oxidate matrix phase but the mineral form of this elements are not known.

Selenium and tellurium occured preferentially in the Ag-Cu selenides where tellurium substitutes for selenium structure (26). A small amount of both elements also occurs in the oxidate matrix phase. Silver is present in a leach product as euhedral crystals of Ag_2SO_4 , as copper-free Ag_2Se and as an oxidate matrix phase different compositionally from that in the raw anode slimes. Tellurium is leached from the original Ag-Cu selenides, but is reprecipitated in the oxidate matrix phase, possibly as Ag-Pb selenite-antimonate-tellurate. The main carrier of Ag in the oxidate matrix is AgCl.

Tellurium is mostly present, possibly as a Ag-Pb antimonate-selenate-tellurate, in the oxidate matrix phase, but some is retained in the Ag_2Se . Silver and gold tellurites were not found (26).

When the slimes are heated at the start of the TBRC refining the chemical makeup of the slimes change. Okubo et. al.(27) studied one of the refining steps and found that mineral composition changes with an increase in temperature, Table 2.1.

Heating	Minerals	Dried	Temperature, OC				
Kate, OC/min			300	400	500	600	700
	CuAgSe	0*	0				
	Ag ₂ Se	0	0	0			
25	CuO*CuSeO3			0	0	0	
2	Ag ₂ SeO3			0	0	0	
1	Ag		0	0	0	0	0
	3CuO*TeO3				0	0	0
	CuO				0	0	0
	CuAgSe	0	0				
10	Ag ₂ Se	0	0	0			
	CuO*CuSeO3			0	0	0	
	Ag ₂ SeO ₃			0	0	0	
	Ag			0	0	0	0
	3CuO*TeO ₃					0	0
	CuO				0	0	0

Table 2.1. The mineral composition change as a function of heating rate and temperature

Note*: Size of circle in Table 2.1 represents qualitative amount of element or compound listed

From Table 2.1 it may be seen that all the selenium is supposed to be completely removed when the temperature in the system reaches 700°C. The chemistry of Se recovery was discussed in (28), where it is shown that Se is generally present in the slimes in the form of either elemental selenium or intermetallic selenides, typically silver selenide. Oxidation of the elemental selenium generally occurs in two steps: selenium is first volatilized and then converted to selenium dioxide (28), Equation 2.1.

$$Se_{(v,\varphi)} + O_{2_{(g,\varphi)}} = SeO_{2_{(g,\varphi)}}$$
 (Eq. 2.1)

Oxidation of intermetallic selenides such as silver selenide, is generally believed to occur as a two stage process. In the first stage silver selenide is oxidized to the selenite, Equation 2.2. In the second stage silver selenite decomposes to either silver or silver oxide plus selenium dioxide, Equation 2.3-2.4. The reactions are shown below (28).

$$Ag_{2}Se_{(l)} + 1.5O_{2(g=l)} = Ag_{2}SeO_{3(l)}$$
 (Eq. 2.2)

$$Ag_2SeO_{3(i)} = Ag_2O_{(i)} + SeO_{2(i=i)}$$
 (Eq. 2.3)

$$Ag_2O_{(1)} = 2Ag_{(1)} + 0.5O_{2_{(pq)}}$$
 (Eq. 2.4)

During the process of soda slag treatment Te, Cu and Pb are also supposed to be removed from the dore metal. Lead has to be reduced in dore metal to 100 ppm during the second-lead converting step (see Introduction). The third step of the TBRC process is designed to remove Te and Cu from dore metal and retain all the precious metals in the metal phase. There are different efficiencies of impurity removal at each of the different steps of the TBRC process. The results of pilot experiments performed on the TBRC working model are portrayed in Figure 2.1(29).





The conclusion that the most important stage in the recovery or loss of precious metals, is the third stage of the TBRC process - soda slag refining - was made on the basis of research held in Noranda Technology Centre (NTC) and CCR. It was mentioned (30) that precious metals were lost, but the reasons for these losses are not clear.

Scanning Electron Microscope (SEM) examination of dore/matte interfaces in laboratory
experiments at NTC using CCR slimes has revealed small particles of a condensed Ir-Ru phase along the boundary between silver and matte. It was decided that since Rh is similar to Ir and Ru it too may concentrate along the silver boundary (30).

The third soda refining step can be approximately described as a high temperature doremetal - sodium carbonate interaction with oxygen injection into the system (see Introduction). In order to understand what can cause precious metal loss it was decided to investigate the influence of P_{O_2} of the gas phase and the basicity (SiO₂ content) of soda slag on the distribution coefficients of minor elements.

No publications concerning dore metal chemistry, structure or impurities were found in the literature. The only information available was found in binary and ternary phase diagrams.

2.3 Interaction of compounds in dore metal (Phase diagram evaluation).

Chemical analysis of the average dore metal was provided by CCR Noranda Minerals Inc. This analysis showed up to 92% of Ag and 3% of Au in an alloy before the soda slag treatment. So, dore metal before the third step of treatment is a silver based alloy with a lot of impurities, the biggest one being Au (Table 3.3). According to binary diagram (31) the equilibrium phases of the Ag-Au system are liquid and face centred cubic continuous solid solution, which shows the short range order, expected from the negative sign in the enthalpy of mixing. Two possible intermetallic phases exist: Ag_3Au , AgAu.

The other element present in dore metal in significant amounts (0.5%) was Pd.The Ag-Pd system shows complete miscibility at all compositions (32). However, irregularities have been observed in hardness, electrical resistivity, and strain sensitivity measurements over the concentration range 40 to 65 at.% Pd below 1200°C. These irregularities were attributed to the existence of possible intermetallic compounds-Ag₂Pd₃ and AgPd by(33,34). It was suggested that these phases could not be detected by X-ray analysis because of similar atomic scattering factors for Ag and Pd.

The thermodynamic properties of Ag-Pd solid solution, which shows negative deviation from ideality (35), may also be used to support speculation about an interaction of a similar kind. However, the authors (32) believe that the evidence for an intermetallic phase is inconclusive.

As already mentioned, a high amount of precious metals was lost on the third refining step, especially Ag and Rh. The Ag-Rh system was investigated by A.A.Rudnitskii and A.N.Klotinskaya (36). A rather wide region of immiscibility was found in the liquid state. It was experimentally established that the solid solubility of silver in rhodium is about 5 wt%, which increases on raising the temperature and at 1400°C amount is about 10% Ag. The solubility of Rh in silver is extremely small.

The other pair of elements reviewed were Au and Rh (37). Rossler (38) found that liquid gold dissolves more than 1% of rhodium, but in solid alloys rhodium is present as free metal. Linde (39) concluded that at 900°C the solubility is about 0.6 at% or 0.3 wt. % of rhodium. Drier and Walker (40), from X-ray examination, found gold-rhodium alloys to consist of two solid solutions, with up to about 2.25 wt.% of rhodium in gold (possibly even 4.5%) and up to 2-4.5 wt. % of gold in rhodium.

According to the results of investigation by A.A.Rudnitskii and A.N.Klotinskaya (36), about 5 wt.% of Au dissolves in solid rhodium and less than 1 wt.% Rh in solid gold; at higher temperatures there is some increase in these values.

Pd-Rh alloys were studied by Tamman and Rosha (41) who found few solid solutions of different compositions. Nemilov et al.(42) found that mutual solubility of Pd and α -Rh is limited. Raub (43) found that solid solution in the system decomposes below 8500 C with the formation of face-centred cubic lattices of different parameters.

It has been established (44) that the unlimited solubility of Pd in Ag becomes very limited when more than 1 wt. % of the third component, Rh, is added.

Also it was found (45) that the unlimited solubility of palladium with gold becomes very limited when more than 1% of the rhodium is added. When more than 40 wt.% of palladium is added to the binary Rh-Au alloys, the liquid immiscibility region vanishes.

The other two elements present in dore metal in noticeable amounts before the refining step were Se (0.5%) and Te (0.2%). The possible phases of Ag-Se system (46) include: the liquid, possibly with two miscibility gaps; two solid phases - fcc (Ag), hcp (Se), and Ag₂Se, with two polimorphic modifications. The solubility of Se in solid Ag is very limited; it was reported that an alloy with 0.27 at.% Se is heterogeneous after cooling from the melt.

The Ag-Te system (47) includes a liquid with a miscibility gap and five solid phases - fcc (Ag), hexagonal (Te), AgTe, $Ag_{1.9}$ Te, and Ag_5 Te₃. Ag_5 Te₃ forms by a peritectic reaction between Ag₃Te and a liquid more rich in Te. Ag₅Te₃ has been described in various ways; namely Ag₃Te₂, Ag₁₂Te₇, Ag₇Te₄, Ag_{1.6}Te. Two different crystallographic structures are thought to exist. Hexagonal α - Ag₅Te₃ transforms into the 6 form at 2950C in the presence of excess Te. Ag_{1.9}Te is reported to exist in a narrow composition range (34.35 to 34.7 at % Te) between 120 and 4600C. Below 1200C it decomposes to Ag₂Te and Ag₅Te₃.

Room temperature examination of the Rh-Se system by X-ray powder diffraction was conducted by Rummery and Heyding (48). Eleven phases were observed. The compounds $RhSe_{2-x}$ and $RhSe_{2.67}$ have defect pyrite lattices. Authors (49-50) showed that Rh-Se and Rh -Te systems can contain compound with different types of lattice:

- Se
 RhSe2
 : IrSe2 type

 Rh1-3Se2
 : FeS2-p type, homogeneous range

 Rh3Se3
 : Prototype
- TeRh1+uTe2: Cd(OH)2 type, homogeneous rangeRh1+uTe2: FeS2-p type, homogeneous rangeRh3Te3: Rh3Se3 type

Geller (51) describes three phases: RhTe (NiAs type), RhTe₂ (FeS₂-p type) and RhTe₂ (Cd (OH)₂ type). However the only phase properly characterized with respect to composition and structure is Rh₃Te₂ (52,53).

The most Rh rich phase in the Rh-Te system appears to be Rh₃Te₂. This phase exists at temperatures above 550°C and exhibits no appreciable range of homogeneity. Below 550°C

Rh₃Te₂ disproportionates into Rh (no solid solubility of Te in Rh can be detected) and a phase of approximate composition RhTe_{0.9} (structure unknown). The latter does not appear to exist above 559°C where disproportionation into Rh₃Te₂ and an"NiAs-like" phase occurs. The NiAs type phase that Geller (51) reported to be of equi-atomic composition is, in fact close to RhTe_{1.1} [hexagonal; a=3.987(1), c=5.661(1)A] with only a very narrow range of homogeneity.

This matching of the crystal structure possibly explains why Rh is present in a phases containing mainly Cu, Te, and most importantly Ni. According to the phase diagram, the most probable composition of Rh -Te component is Rh_3Te_1 .

The Rh-Se and Rh-Te systems differ from the others by forming two compositionally different FeS_2 -p-like phases of which $Rh_{1.4}Se_2$ and $Rh_{1.4}Te_2$ exhibit broad ranges of homogeneity. Although Rh_3Se_3 and Rh_3Te_3 have well defined stoichiometric compositions, they differ from their homologies in the degree of rhombohedral deformation and also by undergoing peritectic decompositions rather than order-disorder transformations at higher temperatures.

The system Ag-Pb is a eutectic type with limited solid solubility at both the Ag and Pb sides of the diagram (54). Extrapolation of the data suggests zero solubility of Pb in Ag at 2000C, 0.3 at.% solubility was measured at this temperature by thermoelectric power measurements (46). The solid solubility of Ag in Pb is very restricted; the maximum solubility was reported as 0.19 at.% at the eutectic temperature.

Solid solubility of Cu in Ag exists and was reported to be about 8-9 wt.% of copper at 779°C (the eutectic temperature), strongly decreasing with the decreasing temperature (55). At 200°C solubility of Cu in Ag falls to zero.

Copper may be one of the possible carriers of Rh and other precious metals to the slag. The equilibrium phases in the Cu-Rh system are: the liquid and the face-centred cubic phase which forms a continuous solid solution between copper and rhodium at high temperature and decomposes at lower temperatures into two face-centred-cubic solid solution phases, one rich in copper, and the other rich in Rh (56). The system is characterized by the presence of an isomorphous solid across the entire diagram in the temperature region immediately below the solidus. Based on thermal, microstructural, X-ray, and hardness results, (57) postulated a limited solubility of the components with approximately 0 to 20 and 90 to 100 at.% Rh, respectively, and a peritectic reaction at about 1100°C. No experimentally measured thermodynamic data are available on the Cu-Rh system.

The equilibrium phases in the Cu-Pd phase diagram are: the liquid and fcc continuous solid solution, ordered Cu₃Pd and ordered CuPd. The ordering process was investigated in a Cu-41.3 at.% Pd alloy by electron diffraction and metallography. Results (58) showed that the ordered phase forms by nucleation along the grain boundaries of the parent disordered phase and subsequent growth of the randomly oriented nuclei.

The Pd-Pt system forms a continuous solid solution. The existence of a miscibility gap in the solid state with the critical point at 770°C based on the difference of the melting points of Pd and Pt was predicted (59).

2.4 Oxidation of precious metals

One of the factors employed in the third step of the TBRC process is oxygen injection. Thus, oxidation of precious metals has to be reviewed.

The oxidation of precious metals was discussed in (60). High temperature oxidation of Pt group metals results in the formation of volatile oxides. The evaporation of which considerably increases the metal losses in oxygen-containing atmospheres when compared with high vacuum or inert atmosphere conditions. Solid or liquid oxide scales cannot be formed at high temperature because the dissociation pressures of the oxides are higher than latm, Table 2.2.

Table 2.2. Dissociation temperature of platinum- group metals in oxygen (latm).

Oxide	RuO ₂	Rh_2O_3	PdO	Ir	Pt	OsO ₂
Temperature, °C	1580	1140	877	1124	650	-

In Figure 2.2 the metal losses are compiled for the oxidation of platinum group metals in oxygen or air of atmospheric pressure. The straight full line represents the pure metal evaporation in high vacuum. The dashed line 2-3 orders of magnitude below the vacuum curve gives the estimation of the vacuum evaporation in an inert atmosphere of atmospheric pressure. The metal evaporation rate is decreased by the effect of the inert gas molecules in the gaseous boundary layer. Differences in evaporation rate of several orders of magnitude can be caused by the surface of the sample, geometry and size of the sample, the equilibrium conditions and whether the oxidised molecules have enough energy to leave the surface or not.

From the results of (60) it can be seen that Pt, Rh and Pd show the best oxidation resistance, Ru and Ir have markedly higher oxidation rates, and Os oxidizes most rapidly. This order corresponds to the equilibrium vapour pressure of the volatile oxides, thus pointing to the fact that the high temperature oxidation of the platinum group metals is governed by the equilibrium conditions of the oxide formation reaction.





Figure 2.2 Pulladium losses in oxygen (665 mbar) and vacuum as a function of temperature.

Figure 2.3. Platinum losses in oxygen as a function of oxygen pressure and temperature (61)







Figure 2.5. Comparison of the metal losses during high temperature oxidation in air at atmospheric pressure (60).

2.5 Chemical and thermodynamic properties of sodium carbonate

The third step of the TBRC process is designed to remove all the impurities left after the previous treatment, especially, tellurium and copper from dore metal. For this purpose sodium carbonate is used as a slagging agent. No references were found relating to the Dore-metal - soda slag interaction, but some research has been done to understand the nature of sodium carbonate as an addition to regular slags.

The function of sodium carbonate as a slag component was discussed in (62). The thermodynamic stability of soda ash was examined by Toshio Yokokawa and Masashiro Shinmei (62) as a function of the carbon and oxygen potentials of the atmosphere and the basicity of the slag, Figure 2.6. This work identified the high affinity and oxidizing ability of sodium carbonate for phosphorus and sulphur removal from steel.

Maddoks and Turkdogan published series of papers (63) in which they showed that the thermodynamic stability of sodium carbonate depends on the potential of carbon and oxygen according to the decomposition reaction and the basicity of slag. In (64) it was considered that the only basic compound of the slag was Na₂O, and basicity was defined as " - log a_{Ne2O} ", where the standart state was pure Na₂O.

As a result of sodium carbonate decomposition to component oxides, Equation 2.5:

$$Na_2CO_3 = Na_2O + CO_2$$
 (Eq. 2.5)

an equilibrium constant of 10^{-5.7} at 1300°K was calculated. Further calculation (62) provided the following numbers:

- (a) Under 1 atm of P_{CO2}, the activity of Na₂O in Na₂CO₃ is 10^{-5.7}, compared to 10^{-6.5} in Na₂SiO₃.
- (b) If the activity of Na₂O is less than 10^{-5.7} in a slag containing Na₂O, CO₂ starts to boil, This assumes the activity of Na₂CO₃ always to be 1. Thus the slag is capable of accepting oxides more acidic than CO₂ in exchange for the CO₂ dissolved in advance.

Figure 2.6 Stability of Na_2CO_3 as a function of P_{O_2} and C activity (62).



(c) If the if the activity of Na₂O is lower than $10^{-5.7}$ and P_{CO₂} is near 1atm, CO₂ dissolves in a slag. Thus, Na₂O slag is never stronger than 5.7 in basicity. This is a reason why soda ash is a milder base than would be expected.

2.5.1 Influence of silica addition on the properties of sodium carbonate

Silica is added to the TBRC to essentially "flux" PbO in smelting and converting slags. The objective was to make slag with the rough composition PbO:SiO₂. In reality it works to keep slags less aggressive towards refractories, it reduces lead vapour pressure, and it renders the slag more "crushable" when silica additions are far beyond the stoichiometric ideal. However, it is not very easy to know exactly how much silica should be added since the overall composition of revert material is rarely known. This is another reason excess silica is added; to prevent the possible formation of high lead slags (65, 66, 35).

At the third stage of TBRC process silica is never added on purpose, but there is silica left from the previous stages. Because of that it, also very interesting to investigate how the presence of silica can influence the results of the soda refining process. The stability of sodium carbonate slag as a function of P_{o_2} and the basicity of slags were shown, Figure 2.7, and discussed in (62) and the following conclusions were drawn:

- (a) Na₂CO₃ or an appreciable amount of dissolved CO₂ in Na₂O slag is stable only in the area ABCDE, Figure 2.7. Beyond this limit CO₂ desorbs from slags or decomposes into gaseous species or dissolves into liquid metal.
- (b) Under the line AB, or in the region V, Na₂CO₃ decomposes into gaseous Na and O₂, the latter acting as an oxidizing agent.
- (c) In the region S and above, Na₂CO₃ loses CO₂. However, Na₂O reacts with SiO₂ to produce a silicate slag.
- (d) After all the silicon is gone from the steel to the slag phase, the oxygen pressure rises and the rest of the impurities start to be oxidised.

Authors (62) suggested that the most effective way of utilization of Na_2CO_3 for the steel making process would be combination of soda ash with another oxidizing reagent such as O_2 gas so that region V may be avoided and the region S can be realised as soon as possible

Figure 2.7.

Figure 2.7 Stability of Na_2CO_3 and Na_2O slags as a function of P_{O_2} and the basicity of the slags (62).



2.6. Changes in oxygen potential in slag and metal during the soda ash treatment.

Several publications were found on the measurements of oxygen potentials during the soda ash treatment of liquid iron (67,68,69). Nagata and Goto (67)found that the oxygen potential decreases markedly in slag, gas, and at the slag/metal interface during the treatment, while the oxygen potential in a metal phase remained essentially constant. Other investigations (68), however, concluded that the oxygen activity in the metal phase decreases during the treatment. The oxygen activity was influenced by furnace atmosphere (69).

Immediately after soda ash addition the bath temperature dropped about 70°C due to the endothermic nature of the soda ash decomposition.

Desulphurisation and dephosphorization effect of soda ash on molten iron was discussed in work of Murayama and Wada (66). It was found that the oxygen activity in the melt was increased immediately after the soda ash addition, decreased rapidly to the minimum value, then increased gradually.

2.7 Copper recovery by sodium carbonate (Cu,O-SiO₂-Na,X System $X = O_1 CO_2$)

Research on slag-metal and slag matte equilibria was carried out by Akira Yazawa (70). Figure 2.8 illustrates the liquid isotherms for the $Cu_2O-SiO_2-(Na_2CO_3 + Na_2O)$ system equilibrated with liquid copper at 1250°C (71). Na₂CO₃ was used as a starting compound, but remained as carbonate just in a region low in SiO₂ and Cu₂O contents. The amounts of CO₂ dissolved in the melt in this region are also shown in top left of Figure 2.8. The prominent feature of this system is the existence of two miscibility gaps, one between carbonate and Cu₂O - Na₂O oxide, and the other between sodium silicate and cuprous oxide. Miscibility gaps between sodium carbonate and oxides are also observed in other systems (72-73).

In the practical use of the soda slag in the copper refining processes, the copper content in slag is of great concern and may be evaluated quantitatively by the iso-activity lines of $CuO_{0.5}$ illustrated in Figure 2.8.

Figure 2.8. Liquidus isotherm and iso-activity lines of Cu_2O at 1250°C for the system of Cu_2O -SiO₂-Na₂X (X = O, CO₃) equilibrated with liquid copper under a flow of argon gas. The figure in top left represents CO₂ content in the carbonate-oxide melt, (70).



Copper content is plotted in Figure 2.9 as a function of oxygen potential and the molar ratio of $Na_2X/(Na_2X + SiO_2)$ in slag. Dissolution of copper as cuprous copper is confirmed from the slopes and lines, and the region of two miscibility gaps are recognised in the upper right of the figure. The content of copper decreases with decreasing Na_2O in the silicate as shown by solid lines, and also decreases with increasing carbonate as illustrated by dashed lines.

Figure 2.9 Dissolved copper in liquid silicate (solid lines) and carbonate (dashed lines) plotted against log P_{o_2} at 1250°C



Akira Yazawa, in a review paper (70), pointed that in the refining process of liquid metals, iron is not necessarily an indispensable component, and slag systems free from iron oxide have recently received attention of many metallurgists. The behaviour of group V A elements in soda slag systems is one of the most interesting subjects, because of the necessity of control of distribution of these elements in a metal-slag-gas systems.

Some investigations indicated that the distribution ratios of antimony are related to oxygen potential, that distribution ratios in the sodium silicate slag containing rather high silica have the same order of values as in ferrite slags. High removability of antimony is expected with highly basic sodium silicate slag or $Na_2O-Na_2CO_3$ flux. It is note worthy that the distribution ratio of V-group elements in plain sodium carbonate is not so high under lower oxygen potential, but increases markedly with the increasing oxygen potential. The dissolved species of antimony in sodium carbonate seem to change from trivalent to pentavalent depending on oxygen potential, while predominant species may be trivalent in other slags (70).

2.8 The Thermodynamics of Copper Fire-Refining by Sodium Carbonate.

Interesting research was performed by Kojo, Taskinen and Lilius on the thermodynamics of copper fire refining by sodium carbonate (74). They examined the behaviour of Se, Te and Cu in soda slag.

Figure 2.10. Observed and calculated slag-metal distribution coefficients for Se and Te between liquid Cu and sodium carbonate.



The equilibrium distribution for tellurium in oxidizing conditions is favourable for effective removal, but selenium can be refined from crude copper with difficulty, its distribution coefficient remaining close to unity even at oxygen saturation of the alloy. However, the thermodynamic equilibrium favours the removal of both selenium and tellurium in an anionic form, their slag metal distribution coefficients, $L_{Me}^{Dm/SS}$, being greater than 1000 in reducing conditions at $P_{o_{n}} = 10^{-15}$ bar, as shown on Figure 2.10

Figure 2.11 Observed and calculated slag/metal distribution coefficient for Sb, As, and Cu between liquid copper and sodium carbonate at 1200 °C (74).



As Figure 2.11 clearly shows, the slagging of copper in refining is insignificant. At oxygen saturation and in contact with pure copper, the solubility of copper in sodium carbonate slag is only 0.85% (75) and copper losses in sodium carbonate are of a chemical nature. Copper content tends to increase in decomposed Na₂O - Na₂CO₃ melt (71).

Above $P_{0_2} = 10^{-7}$ bar selenium and tellurium were found to exist in the soda slag as tetravalent, SeO₂ and TeO₂, and copper as monovalent cationic species, Cu₂O. Under more reducing conditions selenium and tellurium dissolved in the slag as a divalent anionic species: Na₂Se, Na₂Te.

It can be concluded that:

- 1. No research has been carried out on the behaviour of minor elements during the dore metal soda slag interaction.
- 2. Research performed for other types of the processes claims the loss of all the precious metals as a mechanical loss, which is increasing with the increase of slag viscosity.
- 3. The oxidation of precious metals is possible.
- 4. An increase of oxygen potential influences soda slag chemistry.
- 5. Silica presence in sodium carbonate also changes its chemistry and ability to interact with metal phase.
- 6. Dore metal is a silver based alloy with Au, Pd and Pt, having intermetallic phases as an impurities.
- 7. To understand the nature of interaction between dore metal, soda slag and oxygen, research based on different SiO₂ presence in slag, different P_{O2} of the gas phase and different types of dore metals is required and forms the basis for the remainder of this thesis.

Part 1. Distribution of minor elements between dore metal and soda slag

3.1.1 Introduction

The main purpose of the experimental program was to determine the distribution of minor elements between dore metal and soda-slag under the influence of different P_{O_2} and SiO₂ content in soda-slag. The influence of P_{O_2} was studied by fixing the P_{O_2} using a CO/CO₂ gas mixture and an Ar/O₂ gas mixture in the system. The influence of the SiO₂ content in soda-slag on the distribution of minor elements was studied by additions of 5 or 10 wt% of SiO₂ to the soda slag. Another variable was the Dore-Metal (DM). It was considered in order to determine if components that are usually not taken into account during TBRC- process assaying, can influence the distribution of minor elements. Each experimental run used four crucibles simultaneously. Three of them contained synthetic dore-metal (SDM) made from chemically pure components. The fourth one contained commercial dore-metal (CDM) taken from an operating TBRC. Synthetic DM was produced to match the average assay of commercial dore-metal before the last stage of the TBRC process, the soda-slag treatment.

After the experiments, samples of dore metal and soda slag from each test were chemically analyzed by Atomic Absorption Analysis for Au, Ag, Pd, Se, Te, Rh, Cu, Pb, C and some of the samples were analyzed by Scanning Electron Microscopy to determine the microstructure and composition of the various phases present.

The parameters that were fixed during experiments were:

- 1) Temperature inside the furnace 1200°C
- 2) Gas flowrate 100 ml/min
- 3) Rates of cooling and heating

3.1.2 Oxygen pressure in the gas phase

The range of gas phase P_{O_2} was from 10⁻⁸ atm to latm. The gas ratio for these conditions was calculated by HSC (Outokumpu software for the thermodynamic calculations). From 10⁻⁸ to 10⁻⁴ the gas phase was based on CO and CO₂ at various ratios to produce the desired oxygen pressures. For the gas phase with P_{O_2} from 10⁻² to 1 atmosphere, the mixture was Ar and O₂ at 12000C.

The results of the HSC calculations and the gas phase composition are presented in Table 3.1.

Number	P ₀₂	CO/CO ₂	CO ₂ /CO	Mixture	Ratio
1	1.00E-08	3.27E-02	30.62	30:1	pure
2	1.00E-06	3.27E-03	306.2	CO/CO ₂ +CO ₂	1:10
3	1.00E-04	3.27E-04	3062	CO/CO ₂ +CO ₂	1:100
4	1.00E-02	3.27E-05	30620	O ₂ +Ar	1:100
5	2.10E-01	7.13E-06	140318.5	O ₂ +Ar	21:79
6	1.00E+00	3.27E-06	306200	02	pure

 Table 3.1.
 Compositions of the gas phase calculated by HSC.

The gas mixture CO/CO_2 - 30:1 was specially purchased pre-mixed because it was the easiest way of preparation of the desired gas mixtures.

3.1.3 The slag composition

Slag compositions are listed in Table 3.2.

 Table 3.2.
 Composition of the slags corresponding to the number of the crucible in an experiment.

No. of crucible	I	П	Ш	IV
Composition of slag	pure Na ₂ CO ₃	Na2CO3,95% SiO2, 5%	Na ₂ CO ₃ , 90% SiO ₂ , 10%	pure Na ₂ CO ₃

3.1.4 Dore-metal composition

Compositions of the two types of dore metal are given in Table 3.3.

 Table 3.3.
 Composition of dore metal used for the experimental work.

Type of DM	Au, %	Ag, %	Cu, %	Pb, %	Pd, %	Se, %	Te, %	Rh, ppm	Pt, ppm
SDM 1	3.81	93.4	1.61	0.0308	0.46	0.42	0.18	227	96
SDM 2	3.08	94.4	1.51	0.0264	0.14	0.58	0.21	116	263
CDM	3.1	94.2	1.24	0.11	0.47	0.045	0.36	51.3	332

3.1.5 Experimental apparatus and materials

A silicon carbide reaction tube furnace with an automatic digital program temperature controller, REX - P90, was used, Figure 3.1. Besides the two thermocouples built into the furnace (under the tube and in the middle of heating zone outside the tube), a third one was introduced into the system between the crucibles to control temperature inside the tube (N-type thermocouple with inconel sheath from "OMEGA"). A specially shaped mullite reaction tube was placed inside the silicon carbide furnace. One end of the reaction tube was closed, and gas injection was made through a specially machined gas tight plug placed in the other end. Crucibles used to hold the dore metal and slag were magnesia, $2.54 \text{ cm} (2.54 \times 10^{-2} \text{ m})$ diameter, $11 \text{ cm} (11 \times 10^{-2} \text{ m})$ high, and were obtained from "Ozark-Technology".

3.1.5.1 Crucibles

The high density MgO crucibles used for the experiments were chosen because magnesia refractories are employed in commercial operations as the cheapest and least reactive type of refractories for Dore-metal production. The chemical composition of "OZARK"-magnesia crucibles is presented in Table 3.4.

 Table 3.4.
 Composition of magnesia crucibles used for the experimental work.

MgO,%	CaO,%	SiO ₂ ,%	Al ₂ O ₃ ,%	Fe ₂ O ₃ ,%	B ₂ O ₃ ,%
99.38	0.36	0.14	0.03	0.07	0.01

The high density composition of the magnesia crucible used offers a fine grained microstructure and a low open porosity, which is very important with the presence in the system of such reactive components as Na, Se, Te, Si and O_2 . The bulk density is a minimum of 3.3 gm/cc, or 92% of theoretical. Typical density analyses are 3.45 gm/cc, or 96% of theoretical. Open

porosity is less than 1%. The high density body contains up to 3% of yttrium oxide (Y_2O_3) as a sintering aid in direct substitution for magnesium oxide content.

3.1.5.2 Experimental materials

Synthetic Dore-metal (SDM) was prepared from the pure metals. Silver, gold and palladium were bought from "KITKO" company (a Montreal company specialising in the melting and refining of precious metal scrap). The purity of gold was declared to be 99.99%, the purity of silver 99.99%, and the purity of palladium 99.98%.

Copper ('1.5 wt%), used as an impurity was taken from a vacuum-remelted piece of electrolytically purified copper from CCR with a purity of 99.99+% of copper. A small amount of lead (0.04%) was added. This was cut from a 99,99+% purified lead ingot available in the laboratory.

Tellurium and selenium were obtained from CCR and their purities were 99.99% and 99.97% respectively.

Platinum and rhodium were obtained from platinum-rhodium thermocouple wire.

To make a homogeneous alloy (to ensure that each piece of metallic alloy, used for the experiments, is equal in chemical content and properties), it was necessary to know about the mutual solubility of metals, the temperatures of melting and boiling and the density. Information about the various metals is presented in Table 3.5.

Table 3.5.Order of introducing metals to the alloy during the preparation of the synthetic dore
metal. The crystal structure of the additive is also listed in brackets in the order
column.

Order	Quantity, grams	Element	Temp. of melting, OC	Temp. of boiling, OC	Density, g/cm3
1 (cub)	920	Ag	961.93	2212	10.5
2 (cub)	36	Au	1064.43	3080	18.88
3 (cub)	15	Cu	1063.4	2567	8.92
4 (cub)	5	Pd	1554	2970	12.02
5 (cub)	2.0	Pt-Rh	1772-1966	3827-3727	21.45-12.4
6 (rhomb)	1	Те	452	1390	6.00
7 (cub)	0.1	Pb	327.5	1740	11.3
8 (hex)	2.4	Se	217	684	4.81

3.1.6 Experimental program

The experimental program consisted of the seven runs listed in Table 3.6

For the first two runs synthetic dore metal was prepared in an induction furnace in two steps: melting the basic alloy (precious metals), addition of volatile elements. A graphite crucible with an internal diameter 10 cm (10^{-1} m) and a wall thickness 1 cm (10^{-2} m) was made. Graphite was chosen, because, according to the binary diagrams, none of the participating metals reacted with graphite at 1200°C.

As a first step, all the precious metals were melted together in an open furnace. To make temperature measurements an N-type thermocouple was introduced to the melt, but because of the unexpectedly high temperature of the melt (>1300°C) the inconel sheath of

Table 3.6.	Experimental	program.
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No. of experiment	Type of DM	Type of slag	P ₀₂ of gas phase, atm
1 - 1	Synthetic (SDM)	Na ₂ CO ₃	
1 - 2	Synthetic (SDM)	Na ₂ CO ₃ +5%SiO ₂	2.10×10 ⁻¹
1 - 3	Synthetic (SDM)	Na ₂ CO ₃ +10%SiO ₂	
1 - 4	Commercial (CDM)	Na ₂ CO ₃	
2 - 1	SDM	Na ₂ CO ₃	
2 - 2	SDM	Na ₂ CO ₃ +5%SiO ₂	1.0
2 - 3	SDM	Na ₂ CO ₃ +10%SiO ₂	
2 - 4	CDM	Na ₂ CO ₃	
3 - 1	SDM	Na ₂ CO ₃	
3 - 2	SDM	Na ₂ CO ₃ +5%SiO ₂	1.0×10 ⁻²
3 - 3	SDM	Na ₂ CO ₃ +10%SiO ₂	
3 - 4	CDM	Na ₂ CO ₃	
4 - 1	SDM	Na ₂ CO ₃	
4 - 2	SDM	Na ₂ CO ₃ +5%SiO ₂	1.0× 10 ⁻⁸
4 - 3	SDM	Na ₂ CO ₃ +10%SiO ₂	
4 - 4	CDM	Na ₂ CO ₃	
5 - 1	SDM	N82CO3	
5 - 2	SDM	Na ₂ CO ₃ +5%SiO ₂	1.0×10 ⁻⁶
5 - 3	SDM	Na2CO3+10%SiO2	
5 - 4	CDM	Na ₂ CO ₃	

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No. of experiment	Type of DM	Type of slag	P ₀₂ of gas phase, atm		
6 - 1	SDM	Na ₂ CO ₃			
6 - 2	SDM	Na2CO3+5%SiO2	1 0×10 ⁻⁴		
6 - 3	SDM	Na ₂ CO ₃ +10%SiO ₂			
6 - 4	CDM	Na ₂ CO ₃			
7 - 1*	SDM	Na2CO3			
7 - 2*	CDM without film	Na ₂ CO ₃			
7 - 3*	Splash on top of CDM	Na ₂ CO ₃	2.1×10 ⁻¹		
7 - 4*	Film from surface of CDM	Na ₂ CO ₃			

* Experiment No. 7 was a fast cooling experiment. Samples were taken out of the furnace and air cooled.

the thermocouple melted, thus allowing Ni and Fe to become dissolved in the melt.

The next step of making synthetic dore was the addition of selenium, tellurium and lead. Selenium pills, lead and tellurium (in small pieces) were introduced to the melt and the dore metal was stirred with a graphite rod. The amount of Se and Te was double the amount needed, because these metals begin to boil at 600°C, and hence they are volatilised and not recovered into the alloy.

For the other five runs dore metal was made in a furnace with silicon carbide rod heating elements. Stirring of the melt was manual during the melting.

The commercial dore metal used in all seven runs was obtained from the working TBRC at CCR. The sample material was covered with a 0.5 mm dark film, which surrounded the sample from top and bottom and was very hard to cut. The content of commercial dore-metal and both synthetic dore-metals are shown in Table 3.3.

3.1.7 Description of the experimental procedure

The procedure for a typical run was as follows:

The mullite reaction tube with the closed end was placed inside the silicon carbide furnace. An alumina carriage (designed from an alumina dish to hold crucibles together) with four magnesia crucibles containing dore metal (80 grams) and soda-slag (5 grams) were inserted in the mullite tube, Figure 3.1. Because of the round shape of the closed end of the tube, it was necessary to support the alumina carriage with a refractory fibre cushion in order to prevent cracking of the tube.

Gas or mixtures of gases entered the system through a value on top of the mullite tube at a constant flowrate. The gas flowrate was controlled by gas flowmeters, N1 and N2, Figure 3.1. The open end of the reaction tube was sealed with a water cooling system.

The time-temperature profile for each run consisted of heating, holding and cooling. For the first five hours during the heating period, the system was held under an Ar atmosphere. When the system reached 1200°C the gas mixture with the desired Po_2 was introduced to the system with the same flowrate as the Ar, 100 ml/min. This was considered the beginning of the experiment itself.

Steady experiment conditions were maintained for four hours during which time the gas mixture with the desired Po_2 was introduced to the system. After four hours of experiment, there was a cooling period, of five hours (except for run N7), under an Ar atmosphere.

Temperature measurements were continuous during the heating-experiment-cooling period. Thermocouple T_1 was directly under the closed end of the reaction tube; thermocouple T_2 was at the middle of the hot region (these two thermocouples are part of the furnace temperature control). Thermocouple T_3 incomel N-type thermocouple from "OMEGA" was independent and measured the temperature between the crucibles inside the alumina carriage.

Concurrent measurements of temperatures inside and outside the reaction tube made it clear that between the crucibles the heating process was slower; but during the experiment, the temperature between the crucibles exceeded the furnace controlled temperature by 30-40°C. This



Figure 3.1 Experimental arrangements for the determination of the distribution coefficient between dore metal and soda slag.

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may have been the result of the chemical reactions in the system (if they were exothermic). In addition, the error of temperature measurements at $1200\circ$ C can be as much as 0.75% (9°C), which may also account for different readings from the thermocouples (Temperature Handbook, Omega, vol.28).

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3.1.8 Sample preparation

Following the completion of an experimental run it was necessary to prepare samples for analysis. The first step was to separate metal and slag from the crucible. To do so was quite easy for the metal but difficult for the slag. At the internal crucible surface, a dark (practically black) layer between crucible and metal had formed.

A similar black layer was noticed as an intermediate layer between metal and slag, which were mostly separated easily from each other. For some samples it was a problem to separate metal from slag, because of a sizable intermediate constituent situated between metal and slag, Figure 4.2a. The biggest problem was separation of soda slag from the crucible as a result of chemical reaction between them.

The next step of sample preparation was crushing (the slag samples) and drilling (metallic phase) for analysis.

3.1.8.1 Preparation of the slag samples for analysis

Sampling for atomic absorption analysis:

The preparation of a slag sample had to be done very carefully because of the small amount of slag (~ 5 grams) and the very low content of minor elements which had to be measured.

First of all, it must be mentioned that soda-slag generally consisted of two layers after the

experiment, Figure 4.1-4.2. They were separated by a thin black middle layer, Figure 4.2. Also most of the slags contained droplets of the metallic phase; it was necessary to separate these before assaying. Slags were crushed in an agate mortar and screened through a 150 mesh screen. This procedure was successful in separating most of the metallic droplets.

Sampling for SEM analysis:

Separate pieces of slags were mounted in Quick Mount - self setting resin from Fulton Metallurgical Products Corporation - and dry polished for SEM analysis. Polishing was carried out with silicon carbide paper down to grade 4000. Cleaning of slag samples was carried out in an ultrasonic bath with acetone.

3.1.8.2 Preparation of metal samples for analysis



Sampling for chemical analysis:

To obtain the dore-metal samples from each experiment, drillings were made at different locations of the sample, but not from the top surface because of the cylindrical shape of the sample and the high surface hardness. Also different depths of drilling were used. Five to nine grams of each sample were collected for the analysis. Because of the very hard top surface, drillings were also taken from a section through the sample.

Sampling for SEM analysis:

For the SEM analysis, two parts of the reacted dore metal were examined: the top, covered by a thin black film, and some pieces of slag phase which were not so easy to separate; and a longitudinal section of the dore metal sample that showed the impurity distribution from the bottom to the top of the sample. Pieces of dore metal were cut and polished in three steps: silicon carbide sand paper down to 2400, diamond paste to 0.25 micron and, as a last step, colloidal silica.Samples were kept in a hot air dryer before analysis because of their reactivity with humid air.

3.1.9 Chemical analysis

All the analytical work was done at the Noranda Technology Centre, Quebec, Point Claire. Atomic Absorption Spectrophotometry (AAS) was used for chemical analysis of dore-metal samples. Inductively Coupled Plasma Spectrophotometry (ICP) was used for the soda slag. The analytical error of these analysis was claimed to be $\pm 10\%$.

3.1.10 Optical analysis

As a preparation step for the SEM analysis, optical analysis of the polished samples was carried out. All the phases which could be distinguished by optical microscopy were used as a guide for the SEM work. The results of the optical analysis are presented in Figure 3.3 for samples taken from runs 1 and 2. This optical analysis was sufficient for planning SEM work on all the Runs 1-7.

3.1.11 Scanning Electron Microscope Analysis.

Scanning Electron Microscopy was used to analyze the polished surface of dore-metal and soda slag samples The SEM analysis used Energy Dispersive Spectroscopy with the LINK software analysis system. The purpose of the SEM examination was to distinguish what elements were present in each phase, what was the structure of the phase, and how it formed. Prior to SEM analysis, samples were carbon coated to avoid electrical charging in the sample chamber.

The SEM analysis had some shortcomings concerning the analysis of the impurities in the



Experiment 1-2

Experiment 1-3

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Experiment 2-1





Experiment 2-2



Experiment 2-4



- A beryllium window was used between the sample chamber and the X-ray detector. As a result, light elements could not be detected because their characteristic X-rays do not possess the energy to pass through the window.
- 2) Without oxygen and carbon detection the analysis could not tell if the phase was intermetallic or a mixture of oxides and carbonates. The EDX system of this microscope did not have a light element detector.

Thus, analytical results from the SEM were used qualitatively and not quantitatively.

Samples of dore metal and their corresponding slags were characterized mineralogically to determine the phases present and their morphologies. The mineralogical data were then used to assess possible causes of precious metals loss.

Part 2. Determination of the melting point of soda slags.

3.2.1 Introduction

The second part of the experimental work was designed to determine the melting points of commercial soda slags. It was done to find a correspondence between soda slag composition and melting point of the slag. These experiments used commercial soda slags from CCR with the chemical assays as shown in Table 3.7.

3.2.2 Experimental

These experiments used an apparatus developed in the Department of Metallurgy and Materials Science, University of Toronto. The experimental setup is shown in Figure 3.3.

A small amount ~ 0.5 gram $(0.5 \times 10^{-3} \text{ kg})$ of soda slag contained in a magnesia dish (\sim 2 grams $(2.0 \times 10^{-3} \text{ kg})$) was introduced into the cylindrical heating element made from 0.5 mm $(5 \times 10^{-4} \text{ m})$ thick, platinum strip (diameter $\sim 25.4 \text{ mm} (25.4 \times 10^{-3} \text{ m})$), situated inside a large quartz dome, that had an inlet and outlet for the gas flow and thermocouple. A Pt-Rh thermocouple was positioned 5 mm $(5 \times 10^{-3} \text{ m})$ above the sample. To check the correspondence of the thermocouple readings to the sample temperature, the samples were touched by the thermocouple several times during the experiments, Figure 3.6. Readings did not change. Experiments were held under a flow of nitrogen

The process of melting and crystallization of each sample was recorded by a video camera using a special connection to a microscope set up in front of the sample. Another camera recorded the screen of the thermometer and a Video Cassette Recorder (VCR) allowed simultaneous observation of both views on one screen.

The magnification of the microscope was from 10 to 100 so that it was possible to watch and record the process in detail. Table 3.8 presents the experimental results.

	Chemical composition of the commercial soda slag												
No.	SiO ₂ ,%	Rh,%	Ag,%	Au,ppm	Pd, ppm	Ni, %	Pb,%	Cu,%	Na,%	A1,%	Te,%	Se,%	Pt, ppm
1	4.75	0.19	2.51	264	42.2	0.16	3.43	7.06	12.2	0.54	26,6	1.15	<50
2	3.62	0.33	2.29	267	45.4	939 ppm	1.01	4.45	17.5	0.35	17.9	1.19	<50
3	4.39	0.00118	6,38	28	<3.5	0.11	4.83	8.06	6.14	0.27	25.0	10.1	<50
4	12.23	0.00796	2.39	678	143	0.34	28.3	0.45	1.25	0.7	0.30	0.82	<50
5	10.96	0.23	1.78	393	79.3	0.27	15.5	2.8	7.94	0.64	3.83	0.86	<50
6	4.55	0.0047	16.3	0.36%	505	768 ppm	3.97	9.56	6.13	0.33	21.2	3.92	<50

Table 3.7. Chemical composition of the commercial soda slags.



Figure 3.3 Experimental setup for the determination of the melting point of commercial soda slag.

3.2.3 Description of the experiments.

The experimental work showed that slag 1, with the highest content of Te (26.6 %), had the lowest sintering temperature. Melting of this slag started also at a relatively low temperature (690 \circ C). At 800 \circ C this slag already looked melted but many tiny solid particles still floated on the surface of the melt together with metallic needles. At 940 \circ C all the surface particles were melted. At 1050 \circ C the melting process was complete, Table 3.8, Figure 3.4 a,b,c,d.

No.of	TEMPERATURE, °C							
slag	Sintering	Melting starts	Melting complete					
1	330	690	1050					
2	430	670	909					
3	600	870	1080					
4	750	870	1100					
5	-	812	1000					
6	590	615	1090					

 Table 3.8.
 Melting points and sintering temperatures for the soda slags.

For slag 2, the sintering process started later, at 430°C. At 670°C the process of the volume reduction started and the slag had the appearance of a wetted mass. The first drops of liquid began to separate from the mass at 824°C. At 909°C all the slag was melted but the liquid phase had a few solid particles still floating on the surface, Figure 3.5 a,b,c.
Slag 3 can be characterized as a high selenium slag. This slag showed an interesting behaviour during the solidification process observed at the end of the melting experiment. At 250°C Cu needle growth started and the slag became partly green and partly red. Figure 3.6 presents the heating chamber with molten slag 3 on the magnesia dish. Figures 3.6b and 3.6c show the difference in temperature reading between the regular position of the thermocouple and when it was moved to touch the slag.

Slag 4 had the latest start of the sintering process (750°C). As for slag 3, melting started around 870°C and slag was fully melted at 1100°C. This slag had the highest content of Si and Pb, which made its melting point higher than for the other slags. Also the presence of Si influenced slag viscosity; slag 4 had a drop shape even after the melting process was complete. Growth of some metallic phase from the slag was noticed at 175°C during the solidification period, Figures 3.7 d-e.

For slag 5, it was not possible to determine a temperature when sintering began. At 812°C, the beginning of melting was observed and at 920°C the slag was almost melted, although some particles were still present on the slag surface. At 1050°C, all the particles from the surface had disappered, Figure 3.8a-c. Again, a very active precipitation of Cu from the slag occurred during the cooling period which began at 250°C, Figures 3.8 a-e.

Slag 6 was very interesting because of its high content of precious metals, Figure 3.9 a-g. After the complete melting of slag at 1090°C, a few shiny droplets popped up from the melt and began coalescing, Figure 3.9 c,d. Finally, a big metallic drop formed at the middle of the slag. This droplet solidified at 785°C. Copper needles start to grow from the crystallized slag at 479°C, Figure 3.9e. At 250°C, the same copper precipitation took place from the metallic droplet Figure 3.9 f,g.

It can be concluded that the melting point of the slag increases with the silica content. At the same time the wettability of the magnesia lining by slag is reduced with the increase of silica content in slag.

Slags with a high content of precious metals can be cleaned up by simple remelting of soda slag and subsequent separation of the metallic droplets.













- b) melting started, volume of slag reduced c) slag is melted

Chapter 3.

Experimental.

Part 2



Figure 3.8. Determination of the melting point of soda slag, Slag 5, Table 3.7 d) precipitation of Cu from the solidified slag started at 250°C e) the amount of precipitated Cu increased with the temperature drop. 53



- c) slag melted completely, metallic phase started to separate from the melt.d) with the temperature drop coalescence of small metallic droplet into one big droplet occurs.

÷N



Chapter 3.

Experimental. Part 2

e) solidified droplet of metallic phase

- f) precipitation of Cu started from the metallic droplet at 250°C
- g) metallic droplet covered with the precipitated Cu

CHAPTER 4. EXPERIMENTAL RESULTS

4.1 Results of the chemical assays

Twenty eight experiments (seven runs) were performed with different P_{0_2} of the gas phase and SiO₂ content in the soda-slag. All the samples after the experiments looked different, but there were some similarities also.

The results of chemical analysis for the dore metal and soda slag samples are presented in Tables 4.1 - 4.3. On the base of the chemical analysis, the distribution coefficient between dore metal and soda slag was calculated as follows:

$$L_{Me}^{(Dm/SS)} = \frac{X_{Me_{down make}}}{Y_{Me_{make}}}$$

- distribution coefficient between dore metal and soda slag

- mass % of impurity metal in dore metal

 $Y_{\rm Me_{suis sing}}$

X_{Medan masi}

L_{Me}^{Dm/SS}

-mass % of impurity metal in soda slag.

The calculated distribution coefficients are presented in Table 4.4.

No. of exp.	Au, %	Cu, %	Pb, ppm	Pd, ppm	Pt, ppm	Rh, ppm	Se, %	Te, ppm	SiO ₃ , %	P _{o3}
1-1	3.21	1.01	128	4400	249	4.77	.0226	4.8	0	0.21
1-2	3.26	1.46	211	4400	274	2.7	.0125	4.8	5	0.21
1-3	3.27	0.73	33.5	4500	265	5.3	.0114	4.8	10	0.21
2-1	3.3	0.42	5.75	4600	286	2.7	.0112	4.8	0	1
2-2	3.15	1.04	151	4400	293	2.7	.0117	4.8	5	1
2-3	3.31	0.94	125	4500	278	6.74	.0306	4.8	10	1
3-1	3.38	0.58	5.61	4300	252	2.7	.0132	4.8	0	0.01
3-2	3.29	0.57	29.1	4400	273	3.42	.0415	18.4	5	0.01
3-3	3.29	0.86	5.82	4400	250	8.4	.0263	4.8	10	0.01
4-1	3.22	1.3	156	4100	225	51.7	.025	27.5	0	10 ⁻⁸
4-2	3.18	1.24	111	4200	297	36.3	.0617	155	5	10 ^{-#}
4-3	3.14	1.29	144	4100	261	67.9	.16	468	10	10-*
5-1	3.24	1.63	269	4200	276	2.7	.0124	4.8	0	10-6
5-2	3.29	0.9	116	4300	239	2.7	.0112	4.8	5	104
5-3	3.61	0.89	67.6	4100	363	11.6	.0234	4.8	10	10-4
6-1	3.3	1.0	86.8	4200	368	9.02	.0507	61.3	0	10-4
6-2	3.3	0.77	50.2	4300	332	6.64	.0137	4.8	5	10-4
6-3	3.28	1.08	42.4	4400	350	7.97	.0126	4.8	10	10-4
1-4	3.73	0.45	43.3	5400	374	2.7	.0121	4.8	-	0.21
2-4	3.8	U.48	28.9	5100	417	2.7	.0124	4.8	-	1
3-4	3.59	0.56	33.7	5200	404	2.63	.0114	4.8	-	0.01
44	3.72	1.08	511	4800	424	3.72	.0113	251	-	10-*
5-4	3.79	0.51	93	5200	433	2.7	.012	4.8	-	104
64	3.77	0.80	85.5	5100	434	2.7	.0110	4.8		10-4

Table 4.1Chemical analysis of dore metal samples after the slow cooling experiments.
Nominal SiO_2 content of soda slag and gas phase oxygen potential are also given.

Table 4.2Chemical analysis of soda slag samples after the slow cooling experiments.
Nominal SiO_2 content of soda slag and gas phase oxygen potential are given in
Table 4.1.

No. of exp.	Au, ppm	Cu, %	Pb, ppm	Pd, ppm	Pt, ppm	Rh, ppm	ડર્શ પ્ર	Te, %	Ag, %	C, %
1-1	65.8	1.46	495	<2.0	<6.0	831	4.66	2.16	0.29	7.66
1-2	78.8	3.16	878	3.23	<6.0	795	5.67	1.72	0.62	6.95
1-3	44.8	4.98	1500	<2.0	<6.0	872	5.05	2.07	0.62	5.86
2-1	33.7	4.79	1200	<2.0	<6.0	1100	5.15	2.60	1.05	8.38
2-2	37.8	3.25	904	<2.0	<6.0	744	5.57	2.01	0.58	7.11
2-3	42.1	7.55	2200	2.96	<6.0	729	4.53	2.14	1.05	5.06
3-1	81.3	3.78	1100	<2.0	<6.0	516	5.31	2.32	0.86	7.97
3-2	670	7.58	230	89.1	<6.0	939	4.69	1.62	3.00	5.95
3-3	159	6.64	2100	21.8	<6.0	812	4.48	2.03	1.08	5.50
4-1	32.5	0.093	179	<2.0	<6.0	28.5	6.50	2.05	.0582	7.90
4-2	82.5	0.64	545	<2.0	<6.0	61.9	7.22	2.10	0.20	6.16
4-3	44.3	2.32	2800	<2.0	<6.0	160	6.29	1.95	0.17	5.02
5-1	35.9	0.58	320	<2.0	<6.0	248	6.59	1 .9 4	0.085	7.98
5-2	24.8	1.53	539	<2.0	<6.0	242	6.95	1.71	0.19	7.38
5-3	32.5	5.015	1700	<2.0	<6.0	422	6.92	1.87	0.395	4.75
6-1	32.4	2.82	1200	6.99	<6.0	320	6.81	2.06	0.35	4.75
6-2	30.6	1.26	547	<2.0	<6.0	535	6.26	1.70	0.19	5.55
6-3	90.ċ	0.32	202	5.95	<6.0	235	6.34	1.85	0.204	5.64
1-4	38.7	6.25	13900	11.9	<6.0	1000	.089	5.20	1.04	6.16
2-4	120	8.33	20200	13.9	16.2	885	0.20	6.59	1.53	5.32
3-4	85.7	7.26	18400	11.3	<6.0	997	0.30	6.33	1.04	5.21
44	133	5.16	11200	15.0	11.4	1000	.12	4.51	1.92	5.32
54	86.0	3.70	6700	7.61	<6.0	1100	.34	3.64	0.75	8.02
6-4	56.9	0.39	6400	12.7	<6.0	1100	.12	4.53	0.81	5.61

Table 4.3	Chemical analysis of dore metal & soda slag	samples after the fast cooling
	experiments.	

No. of	f exp	Au, %	Cu, %	РЬ, ррш	Pd, ppm	Pt. ppm	Rb, ppm	Se, ppm	Te, ppm	Ag. %	Ni, ppm
	DORE METAL										
7-1	SDM	3.18	1.14	96.7	4200	334	59.00	587	218	91.90	2.58
7-2	CDM*	3.37	0.99	21.0	4700	379	16.80	49.1	22.4	93.40	2.68
7-3	CDM**	3.47	0.53	128.0	2600	244	12.50	150	281	92.90	10.5
7-4	CDM***	2.85	1.01	49.9	2900	222	21.90	30.9	27.9	94.60	2.87
				so	DDA SLA	NG					
7-1	Na ₂ CO ₃	47.8E-6	0.52	1500	33.8	13.2	1100	56800	19600	0.51	40.8
7-2	Na ₂ CO ₃	9.43E-6	0.34	431	33.3	12.5	298	573	5200	0.21	23.9
7-3	Na ₂ CO ₃	44.5E-6	2.41	10000	33.9	12.5	633	793	40200	1.78	232
7-4	Na ₂ CO ₃	26.1E-6	9.91	28800	72.2	12.5	865	9500	115000	3.15	381

commercial dore metal without dark film

** - splash on top of commercial dore metal

*** - dark film from surface of commercial dore metal

Figure 4.0 Appearance of commercial dore metal provided from TBRC, CCR.



No.of exp	L _{Au} ^{Dm/M}	L _{St} ^{Dm/M}	L _{7%} ^{Dm/96}	L _{Cs} ^{Da/95}	L _N ^{Dar/M}	L ₇₁ ^{Da/M}	L _{Rb} ^{Dra/88}	L _{Te} ^{DwW}	C_, %	SiO2, %	P ₀₁ atın
4-1	990.77	0.00385	0.8715	13.94	2050	37.5	1.814	0.000634	7.9	0	10 °
4-2	385.45	0.00854	0.2037	1.937	2100	49.5	0.586	0.00775	6.16	5	10 ⁻¹
4-3	708.80	0.02544	0.05129	0.556	2050	43.5	0.424	0.024	5.02	10	10*
5-1	902.51	0.001882	0.8406	2.810	2100	46.0	0.010	0.000247	7.98	0	10*
5-2	1326.61	0.001612	0.2152	0.588	2150	39.8	0.011	0.000281	7.38	5	104
5-3	1128.12	0.003493	0.0397	0.176	2050	60.5	0.026	0.000257	4.75	10	104
6-1	1018.51	0.0007445	0.07233	0.3546	601	61.3	0.028	0.002976	4.75	0	10-4
6-2	1078.43	0.002188	0.09177	0.611	2150	55.3	0.012	0.000281	5,55	5	10-4
6-3	362.03	0.001987	0.02099	3.375	739	58.3	0.034	0.000259	5.64	10	10-4
3-1	415.74	0.002486	0.0051	0.153	2150	42	0.005	0.000207	7.97	0	0.1
3-2	49.10	0.008849	0.0126	0.075	49.3	45.5	0,004	0.001136	5.95	5	0.1
3-3	206.91	0.005871	0.0028	0.129	201.8	41.7	0.01	0.000236	5.5	10	0.1
1-1	487.84	0,00485	0.2585	0.691	2200	41.5	0.006	0.000222	7.66	0	0.21
1-2	413.71	0.002205	0.2403	0.462	1362	45.7	0.003	0.000279	6.95	5	0.21
1-3	729.91	0.002257	0.02233	0.146	2250	44.2	0.006	0.000232	5.86	10	0.21

Table 4.4.

No.of exp	L _{Au} ^{Du/86}	L ₅₊ ^{Dm/86}	L ₇₅ ^{Dm/\$5}	L _{Cu} ^{Da/56}	L ₇₄ ^{Dm/86}	L _{T1} ^{Dra/66}	L _{Rh} ^{Den/96}	L _{Te} ^{Da/65}	C., %	SiO ₁ , %	P ₀₁ atm
2-1	979.22	0.002175	0.00479	0.087	2300	47.67	0.024	0.000185	8.38	0	1.0
2-2	833,.33	0.002101	0.1670	0.320	2200	48.83	0.004	0.000239	7.11	5	1.0
2-3	786.22	0.006755	0.0568	0.124	1520	46.33	0.009	0.000224	5.06	10	1.0
4-4	279.69	0.09417	0.04919	0.209	320	70.67	0.007	0.005565	5.32	·	10.4
5-4	440.69	0.03529	0.01388	0.138	683	72.16	0.002	0.000132	8.02	•	104
6-4	662.57	0.094167	0.01336	4.743	402	73.33	0.002	0.000106	5.61	·	104
3-4	418.91	0.03800	0.00183	0.077	460	67.33	0.003	7.6e-05	5.21		0.1
1-4	963.82	0.13595	0.00311	0.072	454	62.33	0.003	0.000923	6.16	•	0.21
2-4	316.67	0.06200	0.00143	0.0576	374	69.5	0.003	7.3e-05	5.32	•	1.0

Chapter 4. Experimental Results.

4.2 Description of the appearance of the samples after the experiment

After the experiments, almost all the crucibles had a chain of tiny droplets of dore metal inside the crucible wall running from the melt surface to the top of the crucible on the side of the crucible closest to the reaction tube. The colour of the crucibles after the experiments ranged from milk white to dark brown-green, dependent on the type of slag and oxidation conditions.

Most of the dark coloured crucibles - from greenish-grey to brown - were the results of the experiments with commercial dore metal. On a few crucibles that contained commercial dore metal, there were droplets of metal at the bottom of the outside of the crucible wall. This suggests that the chain of droplets were formed by foaming of the slag during the high temperature interaction between dore metal and soda slag and also that this reaction was much more active with the commercial dore metal.

For the of the experiments, the separatic¹¹ of dore metal from soda slag was quite easy. Also there were no difficulties with the separation of dore metal from the crucible. However, between the metal and the crucible, there was a black layer which looked the same as the substance present between the dore metal and the soda slag and, sometimes, a film that formed on top of the soda slag.

Metal samples from the experiments No. 1-2, No. 3-1, No. 3-4 and No. 5-3 had a black film on the top surface, Figure 4.1 (a, b). In a samples No. 2-3 and No. 6-4, the black film was not present and the metal surface was clean and shiny. For these tests, slag separated quite cleanly from the metal, Figure 4.1 (c, d).

On top of metal samples No. 1-1, No. 4-2, No. 5-1 and No. 5-2 black buttons were observed, Figure 4.2 (a, b), and these were not easy to separate from the metal surface. They seemed to have a structure different from the slag, but were close in appearance to the black film covering the crucible.

In some of the experiments, it was not possible to separate slag from the metal and some



Figure 4.1. Samples of dore metal after the treatment and soda slag samples with separation layer. With the black film on top surface: a) experiment No.1-2 b) experiment No.5-3. With clean and shiny top surface: c) experiment No.2-3 d) experiment No.6-4



Figure 4.2 Samples of dore metal after the treatment and soda slag samples with separation layers. With the black bump on top surface: a) experiment No.5-1 b) experiment No.5-2. Metal not separated from the slag: c) experiment No.1-1 d) experiment No.4-2

slag was left on metal surface, Figure 4.2 (c, d). The separation of the slag from the crucible was a problem because of the reaction interphase between soda slag and magnesia crucible that was about 0.2 mm thick. This means that magnesia from the crucibles was also reacting with the soda slag and participating in this process.

4.3 Slag separation layers

One of the unforeseen results of the experimental work was the discovery of separation layers in the slag.

Each slag consisted of two layers which were separated from each other with a thin black film. The separated phases had different colours and different appearances, Figures 4.1 and 4.2. The bottom part of the slag was usually darker and more dense. The top part was usually less dense and lighter and its structure has a dendritic appearance. Slags were generally darker with increasing P_{O_2} of the gas phase and SiO₂ presence in slag.

In the slag layers that were identified dore metal droplets of variable size were found to be randomly distributed.

4.4 Results of the SEM analysis

Prior to SEM analysis the visual examination of samples was made with an optical microscope. The samples studied had a very similar grain size which shows that cooling conditions for all the samples were similar. Most of the impurity phases were positioned at the grain boundaries, Figure 4.3.

In order to identify the composition of each phase present in metal and slag SEM X-ray spot analysis of soda slag and dore metal was carried out. The results of the SEM analysis of commercial dore metal before the soda slag treatment are presented in Figures 4.4-4.6 and Table 4.5. The SEM spectral analysis of the phases is presented in Figures 4.A-4.F. Visual examination of the surface of CDM indicated a greyish silver matrix with a number of dark inclusions. At the surface a thin film, (approx. 0.5 mm) was present. The film had a dark grey colour. As a result of the SEM analysis it was found that the film contained at least 12 constituents, Table 4.5. Figure 4.5 shows the general structure of this layer. Also, according to EDS- X-ray spectra analysis, the matrix of dore metal contained minor Pt and Rh, but no Pd (Appendix I).



Figure 4.3. General structure of the commercial dore metal sample before treatment.

Table 4.5.	Elemental	composition	of the	phases	presented	in	commercial	dore	metal
	(Figures 4	.3 - 4.5) befo	re soda	slag tre	atment.				

No. of phase	Elements present in a phase	Figure
1	Ag	4.3 4.4
2	Cu, Si, Pb, Te, also some amount of Ag and Fe	4.4
3	Si and Mg, with some Cu, Ni, Ca, Rh	4.3 4.4
4	Mainly Si with Pb, Cu, Ag, Al, Te, Ba, Fe	4.4
5	Te, Cu, Pb, Ag, with small amount of Si, Cr, Fe, As	4.4
6	Te, Cu, Ag, Pb, with some Fe, Cr, Si, Bi and As	4.4
7	Cu, Sb, Ag, Si, with some amount of S, Fe, Ni and Pb	4.4
8	Si, Pb, Te, Ag, with some amount of Cu, Fe, As	4.3
9	Cu, Te, Ag	4.5
10	Ag, Te, with tiny amount of Se, Cu and Cr	4.5
11	Ag, Cu, Te, with tiny amount of Se and Cr	4.5
12	Ag, Se, with small amount of Cu	4,5



Figure 4.4. General morphology of the dark film covering the commercial dore metal before treatment. Magnification 1000 times.



Figure 4.5. General morphology of commencial dore metal before treatment. Magnification 1000 times.



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Figure 4.B. X-ray spectral analysis, phases: a) 3 b) 4 (Table 4.5, Figure 4.3-4.4)



b) Figure 4.C. X-ray spectral analysis, phases: a) 5 b) 6 (Table 4.5, Figures 4.4)

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The results of the SEM analysis for synthetic dore metal after the soda slag treatment are presented in Figures 4.6 - 4.7 and Table 4.6. The SEM spectral EDS X-ray analyses of the phases are presented in Figures 4.G-4.J

Figure 4.6 presents the synthetic dore metal after the soda slag treatment, Experiment 2-2.

Figure 4.7 shows the synthetic dore metal with the impurity area reacted with the humid air (sample was prepared several hours before the analysis).

Table 4.6.Elemental composition of the phases presented in a synthetic dore metal(Figures 4.6 - 4.7) after the soda slag treatment.

No. of phase	Elements present in a phase	Figure
1	Ag, Au, Cu	4.6
2	Cu, Na, Ag, Ni	4.6
3	Ag, some Mg	4.6 4.7
4	Cu, some Ag, Si	4.6
5	Cu, Ag, some S, Si, Te	4.6
6	Pb with Cu, Si, Ag	4.6
7	Na, Si	4.7



Figure 4.6. Synthetic dore metal after the soda slag treatment.



Figure 4.7 Big bump area in dore metal after the soda slag treatment.







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Figure 4.J. X-ray spectral analysis, phase 7, (Table 4.6, Figure 4.7)

The results of the SEM analysis of the soda slag after Experiment 2-1 are presented in Figures 4.8 - 4.11 and Table 4.7. The SEM spectral EDS X-ray analysis of the phases are presented in Figures 4.K-4.N.

No. of phase	Elements present in a phase	Figure
1	Te, Na, Ni, Cu, Rh, K	4.11
2	Cu, Ag	4.11
3	Se, Si, Na, S, Ag, some Ca, Cl, Fe	4.8 4.10
4	Na, Se, some Si, S, Cl, Ca, Cr, Mn	4.9 4.10
5	Te, Cu, Na, Si, Se	4.8 4.9 4.10
6	Na, Se	4.8 4.9
7	Te, Cu, Ni, Se, Na, Si, S, Fe	4.10
8	Ag	4.10 4.11

Table 4.7.Elemental composition of the phases present in soda slag (Figures 4.8 - 4.11)after the Experiment 2-1.



Figure 4.8. Soda slag after the experiment (Backscattered Electron Image) with the separation intermetallic layer.



Figure 4.9. Soda slag after the experiment (Scanning Electron Image) with the separation intermetallic layer.


Figure 4.10. Intermetallic layer in soda slag after the experiment (BEI). Magnification 500 times.



Figure 4.11. Intermetallic layer and lower part of soda slag after the experiment (BEI). Magnification 100 times.



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Figure 4.L. X-ray spectral analysis, phases: a) 3 b) 4 (Table 4.7, Figure 4.8-4.10)





Figure 4.N. X-ray spectral analysis, phases: a) 7 b) 8 (Table 4.7, Figure 4.10-4.11)

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The results of the SEM analysis of soda slag after reaction with commercial dore metal, Experiment 2-4, are presented in Figures 4.12 - 4.13 and Table 4.8. The SEM spectral EDS X-ray analyses of the phases are presented in Figures 4.0-4.Q

Table 4.8.Elemental composition of the phases present in soda slag (Figures 4.12 - 4.13)after Experiment 2-4.

No. of phase	Elements present in a phase	Figure
1	Si, Pb, Na, Cu, Pb, Cr, Se	4.12 4.12
2	Si, Pb, Na, Cu, Cr, Se, Fe	4.12 4.13
3	Ag, some Si, Cu	4.12 4.13
4	Te, Na, Cu, with some Si, Pb	4.12 4.13
5	Te, Cu, Pb, Si, Na, Fe	4.13







Figure 4.12. The SEM image of soda slag after Experiment N 2-4



Figure 4.13. The SEM image of soda slag after Experiment N 2-4







Figure 4.Q. X-ray spectral analysis, phase 7, (Table 4.8, Figure 4.13)

CHAPTER 5. DISCUSSION.

The experimental work is discussed under three main headings:

- I. Physical observation
- II. Chemistry of the dore metal
- III. Chemistry of the slag

5.1 Physical observation

In the course of the experimental work, several physical effects were noted:

- 1. The formation of a chain of droplets on the inner side of the crucible wall
- 2. The presence of a black film between metal and crucible
- 3. Difference in the ease of separation of the slag from the metal depending upon the experimental conditions; the presence or absence of a dark film on the top surface of the metal.
- 4. Variation in the value of the distribution coefficients of minor elements $(L_{Me}^{Dm/SS})$ caused by physical effects in the system.

5.1.1 Nature of droplet chain on the side wall of the crucible.

It is believed that the chain of droplets observed on the inner side of the crucible wall, closest to the heating element, was a result of the foaming process which occurred during the interaction between dore metal and soda slag on the hottest part of the crucible.

5.1.2 Nature of the black film between metal and crucible.

As previously mentioned in section 4.3, a black film was found between metal and crucible. This film probably consists of intermetallic phases and silica containing compounds such as sodium, magnesium and lead silicates. Similar observations were made by Morrison (79) as a process of "tie up" of precious metals in the dore furnace refractory during the TBRC process. These compounds are the result of interaction between soda slag, crucible lining and intermetallic compounds rejected by the alloy during the temperature decrease.

5.1.3 Difference in the ease of separation of the slag from the metal.

In Chapter 4, the difference in separation of the slag from the dore metal was shown in Figures 4.1 and 4.2. Possible reasons for this variation are discussed below.

As reported in (47, 54, 55), Cu, Pb and Te are virtually insoluble in silver and the solubility of oxygen falls to zero at room temperature (76). As a result, precipitation of Cu that was dissolved in an alloy at higher temperatures occurs with a decrease in temperature. If the system had a low oxygen potential ($P_{0_2} - 10^{-4}$ atm), some pure copper was observed on the surface of metal, Figure 4.1. A sample that was examined in University of Newcastle, England, showed that thin film on top of metallic phase was mainly Cu₂O when P_{0_2} was 0.21 atm (77).

Separation of the slag from dore metal occurred more easily if the slag had a higher content of SiO_2 and was more viscous. A clean metal surface after the experiment was the result of high partial pressure of oxygen and/or the use of commercial dore metal, which was surface contaminated with silicon arising from slimes in different forms from the previous stages (Experimental results, SEM analysis of dark film). This silicon was among first species to react with soda slag and oxygen (66, 74).

On the other hand, low partial pressure of oxygen (Figure 4.2) and the absence of silica in the system (Series 1) created the problem with the slag-metal separation. This

occurred even when the samples were slowly cooled to room temperature.

5.1.4 Variations in the values of the distribution coefficients of minor elements, L_M, D^{m/SS},

The experimental results from the equilibrium studies are summarized in Tables 4.1-4.2, where the alloy and slag compositions are given in weight percent.

The graphs (Figures 5.1 - 5.8) created by the Quattro Pro program from the data base of Tables 4.1 - 4.4, show the following three relationships, as a function of P_{o_2} of the gas phase and the SiO₂ content of the soda slag:

- (a) the dependence of the impurity content in the metal after the soda slag treatment;
- (b) the impurity content of soda slag
- (c) the distribution coefficient ($L_{Me}^{Dm/SS}$) between dore metal and soda slag

The graphs may be divided into three groups, based on similarity of appearance and chemical group:

Au, Pt and Pd

The experimental distribution ratio obtained for the precious metal impurities were recorded in Table 4.4 and plotted in Figures 5.1.c, 5.2.c, 5.3.c. These graphs are line-type graphs, where the Y-axis is an amount of impurity in a phase or $L_{Me}^{Dm/SS}$ and the X-axis presents the experimental conditions, log P_{O_2} . For discussion it is more convenient to plot the $L_{Me}^{Dm/SS}$ of impurities in terms of weight percentage in slag and alloy. As can be seen from these figures, the level of Au in dore metal and soda slag after the experimental values.

One reason for a large analytical value for Au in an alloy might be segregation of Au (31) or the presence of the gold-containing intermetallics in locations where samples were taken for the analysis. As a matter of fact, gold-enriched areas were observed during the SEM X-ray analysis of the samples. Also large changes in values for Au and Pd in soda slag during experimental Run 3 is most likely the result of sampling error.

Scatter in the Ag content of the slag (Run 3), shows that this variation was repeated three times for the elements remaining in solution (Ag, Au, Pd). The cause could have been a slag sample containing droplets of alloy. Disturbance of the cooling arrangements due to a water leak towards the end of Run 3 could have caused an increased amount of droplets in soda slag. Because of this fact there was not enough time for the metallic droplets in the higher viscosity slags (5 and 10% of SiO₂) to settle down. Crystallized slags were seen to contain tiny droplets of silver alloy, and they were not successfully separated during the sample preparation.





I

c)







- 1 pure sodium carbonate,SDM
- 2 5% of silica in soda slag, SDM
- 3 10 % silica in soda slag, SDM
- 4 pure sodium carbonate, CDM



b)





c)









- 1 pure sodium carbonate,SDM
- 2 5% of silica in soda slag, SDM
- 3 10 % silica in soda slag, SDM
- 4 pure sodium carbonate, CDM













a)

Figure 5.6a. Rh content in dore metal as a function of DM type, Po2 of the gas phase and SiO2 content in slag

- 1 pure sodium carbonate,SDM
- 2 5% of silica in soda slag, SDM
- 3 10 % silica in soda slag, SDM
- 4 pure sodium carbonate, CDM









Figure 5.6c Distribution coefficient of Rh between DM/SS as a function of DM type, Po2 of the gas phase and SiO2 content in slag

Note: all the graphs presented are the line -type graphs





a)



- 1 pure sodium carbonate,SDM
- 2 5% of silica in soda slag, SDM
- 3 10 % silica in soda slag, SDM
- 4 pure sodium carbonate, CDM









c)

Figure 5.7c Distribution coefficient of Se between DM/SS as a function of DM type, Po2 of the gas phase and SiO2 content in slag



Se, Te and Rh

The distribution coefficient of Rh, Se and Te between dore metal and soda slag for SDM markedly decreased (100 times) with increasing P_{O_2} from 10⁻⁵ to 10⁻⁶ (Figure 5.6-5.8). Further increase in P_{O_2} did not really influence the L $_{Me}^{Dm/SS}$ of these metals at 1200°C, and the resulting values of L $_{Me}^{Dm/SS}$ were much lower than unity (Table 4.3). This means that impurities were almost completely removed. For the CDM, however, the L $_{Rh}^{Dm/S3}$ did not change so significantly (3.5 times) with increasing P_{O_2} from 10⁻⁵ to 10⁻⁶. The presence of the dark film on the CDM explains this observation since the dark film was enriched with Rh, Te and Se which easily reported to the soda slag. Therefore removal of these elements from the CDM phase (no dark film) would not strongly change the amount of impurities in the soda slag.

The reason for the decreased recovery of Te and Se with increasing amount of these elements in soda slag is due to the increase in slag viscosity and change in the slag structure with the polymerization of the slag (78). This process can cause the slag to act as a obstacle for O_2 transport to the melt in the present experimental setup.

Cu, Pb

The distribution coefficients of Cu and Pb had a tendency to decrease strongly with P_{o_2} increasing from 10⁻⁴ to 10⁻⁴ and then staying constant with a further increase in P_{o_2} , Figures 5.4-5.5. Silica had a strong influence on the distribution coefficients, but only in the P_{o_2} range from 10⁻⁴ to 10⁻⁶, indicating that the mechanism of copper and lead removal changed at higher P_{o_2} .

This was corroborated by thermodynamic calculations of the free energies of interactions of the Me-O-SiO₂ system. The results of Table 5.1 were generated using the following data:

a) $a_{Pb} = 0.00121$, $\gamma^*_{Pb} = 1.1$, $x_{Pb} = 0.11 \times 10^{-2}$ in silver b) $a_{Cu} = 0.048$, $\gamma^*_{Cu} = 3$, $x_{Cu} = 1.6 \times 10^{-2}$ in silver

Data for γ^{o}_{∞} and γ^{o}_{∞} were taken from "Selected Values of the Thermodynamic Properties of Bynary Alloys", edited by Hultgren et al., 1973

- c) Temperature of 1200°C
- d) Silica content in slag of 5 %
- e) P_{0_3} was changed from 10^{-8} to 1 atm.
- <u>Table 5.1.</u> Gibbs energies of reactions between Cu, Pb, silica and oxygen (calculated by the *REACTION* subroutine on F*A*C*T).

No.	P _{o2} , atm	Input to REACTION	$\Delta G_{1200^{\circ}C}$ of reaction, J/mole
1	10 ⁻⁸ 10 ⁻⁶ 1.0 0.127	$Cu + 0.5O_2 = CuO$	+71995.6 +43795.2 -40806.0 0
2	10* 10* 1.0	$Pb + 0.5O_2 = PbO$	+113980.2 +85779.8 +1178.6
3	10 ⁻⁸ 10 ⁻⁶ 1.0 3.2×10 ⁻⁴	$Pb +0.5O_2 + SiO_2 = PbO^*SiO_2$	+92227.9 +64027.5 -20573.6 0

It was not possible to calculate the Gibbs energy for the Cu-O-SiO₂ reaction, because there were no data in a $F^*A^*C^*T$ database for copper silicates.

From the calculations presented in Table 5.1, the following conclusions can be made :

- a) The oxidation of lead is not possible at the offered conditions. Silica in the system promotes the slagging of lead at $P_{o_{\gamma}}$ equal to 3.2×10^{-4} or greater.
- b) Copper can be oxidized only at P_{o_2} starting from 0.127 atm. Increasing P_{o_2} of the gas phase decreases Gibbs energy of the copper oxygen interaction.

From these numbers it was concluded that silica in the system played a vastly more important role for the Pb recovery than increasing the oxygen potential.

The scatter of data for copper and lead in the metal and soda slag can also be seen in Figures 5.4a,b.-5.5 a,b. This scatter can be explained by the possibility of pieces of metal and soda slag enriched in phases containing these elements having formed part of the analytical sample. According to the SEM analysis these phases were distributed randomly, except for the top section of the metal which was richer in impurity phases (Figure 4.5-4.6). Large inclusions (Figure 4.6) in the dore metal may be the reason for the high impurity content detected by chemical analysis.

The same behaviour was observed for the values of Pb and Cu in the soda slag. However this was attributed to the separation of soda slag with an intermetallic layer, i.e. some samples that were analysed contained more intermetallic compounds than others.

Generally the amount of copper and lead decreased in the alloy and increased in the slag with increasing P_{o_2} . Also, the presence of SiO₂ in the slag increased the amount of the impurity metals in soda slag (Figures 5.4.-5.5).

It is concluded that

- 1. The chemical interaction of magnesia crucibles with the system soda slag dore metal was vigorous.
- Better separation of slag from the melt occurred with an increase in the amount of silica in the slag. But at the same time, the increased silica content in soda slag may increase the losses of dore metal in the form of mechanical inclusions (in case of active mixing).

5.2. Chemistry of Dore metal

One of the variables of the experimental work was the type of dore metal. Synthetic dore metal (SDM) was produced by melting pure metals together and commercial dore metal (CDM) was received from a working TBRC before the soda slag treatment.

The results of the experimental work (Table 4.2, Figures 5.1-5.8) show that the amounts of Cu, Pb, Pd, Rh, Te in slags of the 4th crucible (CDM) in each experiment were higher than those in the 1st crucible (SDM).

From the beginning of the experimental investigation, no differences were observed between the appearance of the two types of metals except for the presence of a very hard dark film on the surface of CDM.

5.2.1 The SEM - EDS analysis of the CDM before soda slag treatment

The matrix of the CDM consisted of a Ag-Au alloy (92% Ag and 3% Au, Table 3.3) with some areas of the alloy enriched with gold. Large inclusions which were observed (Figure 4.4, Table 4.5) contained Cu, Te and Ag and were assumed to be Cu_2Te and Ag_2Te The other constituent detected in the alloy, Phase 10, was a phase believed to be Ag_2Te with small amounts of Ag_2Se and Cu_2Te present. Phase 11 (Figure 4.5), contained the same elements as Phase 9, but the presence of Se gave rise to that phase having the form of a needle. Phase 12 was one of the basic components for the dore metal production - Ag_2Se (26,35).

The dark film, covering the CDM, contained eight constituents. Ag, Pb, Cu, Te and Si were the main constituents of the film. The film contained large inclusions of the metallic phase, Phase 1, in which only Ag was detected. According to the chemical analysis, slags of CDM were also enriched in Pd, compared to the SDM, but Pd was not detected in any slag phase. So, the bright inclusions in the dark film were probably Ag-Pd alloy (32). Pd was not detected by X-ray analysis because of the similar atomic scattering factors for Ag and Pd (32), i.e. overlapping in the X-ray spectrum lines.

Phase 2 was a mixture of copper and lead silicates and tellurides. A deep black phase 3 was a product of the reaction between dore metal, soda slag and refractory. This phase also contained Rh and Ni. Phase 4 was a mixture of silicates. Phase 5 was a mixture of Pb, Cu and Ag tellurides. Phase 6 was visually different from Phase 5 only with respect to shape as a result of the extra addition of silica. Copper antimonate, Phase 7, had a needle shape. Phase 8 was a mixture of lead silicates and tellurides with different additions, Table 4.5.

The above description suggests that the dark film was the result of the previous metal treatment in the TBRC and consisted of a complex mixture of intermetallics, which were insoluble in dore metal and also particles of slag from the previous steps of the process. It is believed that this film forms as a result of the solidification process and could be used commercially as an indicator for dore metal purification. As long as this dark film appears on the surface of dore metal sample from TBRC this alloy needs further purification. Use of this method of process control could economize on time and money for analysis during the TBRC process.

The SEM analysis confirmed that the dark film can result in enrichment of soda slag after treatment with the impurity elements.

It is concluded that:

The dark film on commercial dore metal is a result of the solidification process of the dore metal and consisted of intermetallic and slag particles, precipitated from the dore metal during the solidification process. The presence of this film may be used during the commercial process as an indicator of impurity removal.

5.2.2. Nature of the dark film

To clarify the nature of the dark film and the slag separation layer, fast cooling experiments (Run N7, $P_{o_2} = 0.21$ atm) were performed. Results of the experiments and type of metal and slags are presented in Table 4.3.

By comparing the results of experiments N7 (fast cooling) and N1(slow cooling), it can be seen that more Cu, Rh, Se and Te were left in the dore metal during the fast cooling experiments. Correspondingly there was less copper and tellurium found in the rapidly cooled slag (Experiment 7.2- 7.3). However, the amounts of lead and rhodium in slag N7-1 were higher than in slag N1-1. Since these metals appeared in the slags as volatile oxides, it would suggest that there was insufficient time (i.e. cooling rate was too high) for the lead and rhodium oxides to volatilize in the rapidly cooled system.

Another mechanism of Rh removal from the dore metal can also be suggested. Oxygen has a very high solubility in silver (76) and CO_2 from the soda slag (soda slag decomposes into Na₂O and CO₂) also has a tendency to dissolve in a melt (62). At the same time Rh is insoluble in dore metal and therefore must exist as a separate phase (36). It also has unique surface properties which allow Rh to act as a catalyst for gas reactions. Thus, Rh may collect gases which are dissolved in an alloy on its surface. Surface properties of Rh may permit gases to adhere to the surfaces of the Rh phase and then float the Rh or Rhcontaining particles to the surface of the dore metal, even though the density of Rh is higher than the density of silver alloy. This process is more likely to take place during the cooling period, as the solubility of gases in Ag decreases strongly with decreasing temperature (76).

A similar mechanism may operate for other insoluble impurities as Cu, Te, Pb, or intermetallic compounds formed in the system. These impurities are not as active as catalysts for the gas reactions, but their density is lower than the density of dore metal. Thus these impurities will try to leave dore metal by simply floating. Rising gas bubbles will help to bring the particles up. The higher impurity concentration found near the top surface of the dore metal as observed by optical microscope gives support to this hypothesis. As was found by the SEM analysis of the intermetallic layer in the slag and the dark film covering CDM, Rh was present in two types of phases. In both phases Rh was accompanied by Ni, Te, Mg and Cu. This is to be expected since Pt-group metals all report to the Ni phase during the commercial processing of Cu-Ni ores (89), and only Ni has a complete solid solution with Rh at all temperatures up to the liquidus (80).

Another notable observation concerning the rate of cooling and influence of the dark film on the impurity distribution can be made by comparison of tests N 1-4 and N 7-2 in which P_{O_2} remained 0.21 atm. It was seen that 20 times more Cu, 50 times more Pb, 4 times more Rh, 10 times more Te, 5 times more Ag and 15 times more Se reported to the slag phase in Experiment N1-4 (slow cooling and the presence of a dark film over dore metal) than in Experiment N7-2 (rapidly cooled, dark film was not presented), Table 5.1.

	Au, ppm	Cu, %	Pb, ppm	Pd, ppm	Pt, ppm	Rh, ppm	Se, ppm	Te, %	Ag, %
	Soda slag								
N1-4	38.7	6.25	13900	11.9	6	1000	8900	5.2	1.04
N7-2	9.43	0.34	431	33.3	12.5	298	573	0.52	0.21
	Dore metal								
N1-4	3.73%	0.45	43.3	5400	374	2.7	1210	4.8	-
N7-2	3.37%	0.99	21	4700	379	16.8	49.1	22.4	93.4

 Table 5.2
 Comparison of the experimental results for slow cooled and fast cooled experiments.

The hypothesis that the levels of insoluble impurities (Cu, Te, Rh) were reduced in the dore metal by slow cooling is supported by the results given in Table 5.1. It can be seen that in the fast cooled sample Cu, Te and Rh were present in higher amounts than in the slow cooled sample by factors of 2, 7 and 5, respectively.

ς.

For Pb and Se, both metals were found in higher quantities in the dore metal phase of the slow cooled experiment. The disparity in the behaviour of these insoluble impurities may be attributed to a removal mechamism that is different from that for Cu, Te, and Rh. Lead and Se as well as their oxides are easily volatilized.

Experimental observations indicated that a distinct intermetallic layer separated the slag phase of the slow cooled tests into two regions (Chapter 4); this layer appeared more readily in the presence of dark film material on the CDM. It is believed that separation of the slag into two layers impeded the removal of the Pb and Se from the dore metal because the dark film material acted as a physical barrier to the dissolution of oxygen into the melt and hence the volatilization of Pb, Se and their oxides into the gas phase.

The absence of the black film meant that the removal of Pb and Se from melt to the slag was quite efficient. At the same time, without this film there was no silica present in the system and thus it was much easier for Pb and Se to interact with oxygen and leave the system in the form of volatile oxides.

Chemical analysis of the splash on top of the commercial dore metal (as received from CCR) and soda slag analysis, Experiment 7-3, showed high amounts of Pb, Rh, Ni, Se and, especially, Te (281ppm compared to an average 4.8 ppm for the metal). These results also support the hypothesis that impurities may be transported out of the metal during the temperature drop with the help of gas bubbles.

5.2.3 General mechanism of impurity removal

Molten silver dissolves as much as 200 times its volume of oxygen gas, probably as elemental oxygen (1), with a maximum dissolution of 2.09 at% or ~1.8 wt% of O_2 , occurring at 939°C (76). The solubility of oxygen decreases with decreasing temperature and reduces to zero at room temperature.

The dore metal used in these experiments contained more than nine elements many of which are mutually soluble, e.g. Ag and Pd, Ag and Au, Pt and Pd, Pd and Rh, according to binary phase diagrams (31,32,45,59). Both Pb and Cu exhibit a small solubility in Ag which decreases to zero at 200 °C (54, 55).

Solubility of oxygen, X _o	P ₀₂ , atm	Temperature, °C
0.01635075	1	1200
0.00748	0.21	1200
0.001633	10-2	1200
0.00016328	10-4	1200
1.16328 E-5	10-6	1200
1.16328 E-7	10-8	1200

Table 5.3.Solubility of Oxygen in Liquid Silver, for different Po2 calculated byTK-
solver.

Work performed by Rudnitskii and Khotinskaya on the Ag-Pd-Rh and Au-Pd-Rh ternary systems show that the wide solubility region in binary systems can vanish even by adding as little as 1 wt % of a third component (44, 45).

The appearance of different phases on the melt surface during the slow cooling period can be explained by the decreased solubility of certain elements in silver, thus forcing them to leave metal as the temperature drops. Even if some intermetallics were more dense than the alloy they could float with the oxygen bubbles, which also need to leave the system during cooling. This gas can also carry impurities from the metal to the metal surface where they are incorporated into the soda slag.

It can be concluded that:

Impurities may be removed from dore metal by floating, especially with the help of dissolved gases, during slow solidification.

5.2.4 Chemistry of minor element interaction with oxygen

Au, Pt and Pd

In general, Au and Pt assay in dore metal and soda slag did not noticeably change with an increase in the oxygen potential. This corresponds to the results of H. Jehn(60) that Pt and Pd are among the metals with the best oxidation resistance. The amount of palladium left in the metal increased with increasing P_{o_2} (Figure 5.13). This also corresponds to the research results of (60), which show that palladium evaporates more easily with less oxygen in a system, but does not have a tendency to form oxides under these experimental conditions.

Gibbs energies of the possible oxidation reactions were calculated by $F^*A^*C^*T$ for Au, Pt and Pd using the following conditions: $P_{0,} = 1$ atm, $\gamma^*_{Au} = 0.354$, $\gamma^*_{Pd} = 0.14$

 $2Au + 1.5O_2 = Au_2O_3$ $\Delta G_{1200^{\circ}C} = 491388$ Jmole(Eq. 5.1) $Pd + 0.5O_2 = PdO$ $\Delta G_{1200^{\circ}C} = 50528$ Jmole(Eq. 5.2) $Pt + O_2 = PtO_2$ $\Delta G_{1200^{\circ}C} = 158598$ Jmole(Eq. 5.3)

At 1200°C the Gibbs energy of formation for these reactions is positive, indicating that the oxides of these metals are not likely to form. It is possible to conclude from the thermodynamic data that these metals are present in the slags in the form of metallic or intermetallic inclusions.

It can be concluded that:

To avoid losses of Au, Pt and Pd in the soda slag, it is necessary to increase the time for the system to settle down.

Se, Te and Rh

Se, Te and Rh contents in synthetic dore metal markedly decreased (Te-100 times, Se-10 times, Rh-25 times) with increasing $P_{0_{1}}$ of the gas phase from 10⁻⁴ to 10⁻⁴ atm. It

* Data were taken from "Selected Values of the Thermodynamic Properties of Binary Alloys", American Society for Metals, 1973 should also be noted that further increase in P_{O_2} slightly decreases the amount of impurity left in the metal. The same dependence was seen for CDM. However, for CDM the amount of Rh decreased only 3.5 times with P_{O_2} increase from 10⁻⁸ to 10⁻⁴ atm. This implies that Rh is present as different compounds in CDM and SDM. This hypothesis may be supported by the SEM analysis of the slag and dark film on dore metal: Rh found in CDM dark film was present as an impurity in the form of a silicate-base phase, while in the intermetallic layer in the slag on SDM it was detected as a tellurium based compound, possibly (Na, Rh)₂Cu₂TeO₆.

Assuming that Rh appeared in the alloy in the form of insoluble impurities - metallic Rh particles or intermetallics RhTe (NiAs - prototype, hexagonal structure (51), the following reaction and thermodynamic analysis was performed on $F^*A^*C^*T$ for Rh removal (a _{Rh} = 1, because Rh is practically insoluble in silver alloy, $P_{o_2} = 1$ atm):

$$Rh_{(i)} + O_2 = RhO_{2_{(ge)}}$$
 $\Delta G_{1200^{\circ}C} = -227837 \ Jmole \ (Eq. 5.4)$

This reaction shows that rhodium can leave the system in a form of a volatile oxide RhO_2 , and the Gibbs energy of this reaction is so high that it is not possible to keep Rh inside the dore metal when P_{O_2} of the gas phase exceeds 10⁻⁴ atm. Experimental data, Figure 5.6, support this analysis.

Selenium removal by oxygen may occur according to the following chemical reactions (28):

$$Se_{(gen)} + O_{2} = SeO2 (gas)$$
(Eq. 5.5)
$$\Delta G_{1200°C} = -106778.6 Jmole$$

$$Ag_2Se_{(t)} + 3/2O_2 \Rightarrow Ag_2SeO_3^*_{(t)}$$
 (300-6000C) (Eq. 5.6)
 $AG_{corr} = -11378\&0 \ Jmole$

$$Ag_{2}SeO_{3(\mu)} \Rightarrow 2Ag_{(\mu)} + 1/2O_{2} + SeO_{2(\mu)} *(550-650 \circ C)$$
(Eq. 5.7)
$$\Delta G_{corrc} = 67269.6 \ Jmole$$

$$2Ag_{(4)} + 1/2O_{2} + SeO_{2} \Rightarrow Ag_{2}SeO_{3(4)} *$$

$$\Delta G_{(4)} = -67269.6 \ Jmole$$
(Eq. 5.8)

* ΔG_{1000C} for this reaction could not be calculated (data are not present in a database of F*A*C*T or HSC for temperatures higher than 300-500°K and there is no data for the liquid phase).

Summarizing Equations 5.6 and 5.7 :

$$Ag_{2}Se + O_{2} = 2Ag + SeO_{2}$$
 (Eq. 5.9)
 $\Delta G_{4000C} = -465185 J/mole$

The process of selenium removal in dore metal probably follows Equation 5.9. As described in (28), at temperatures above 580°C silver selenide decomposes directly (Eq. 5.9), or with the formation of silver selenite (Eq. 5.8). The decomposition process was considered reversible (Eq. 5.7-5.8)(28). But according to the $F^*A^*C^*T$ calculations AG_{corc} of the reaction (Eq 5.7) is positive and according to research (27) $Ag_2SeO_{3(r)}$ does not exist in slimes above 700°C. Thus, selenium removal at temperatures higher than 700°C must occur mostly according to Equation 5.9.

As shown in (81), the chemistry of Te removal is based on the reaction:

$$Cu_2Te + Na_2CO_3 + 2O_2 = 2CuO + Na_2TeO_3 + CO_2^*$$
 (Eq. 5.10)

X-ray analysis of commercial soda slag did not show the presence of Na_2TeO_3 in slag, Appendix II. In a literature (90, 91, 92), Na_2TeO_3 was claimed to be present in an aqueous solution. $Na_2Te_4O_9$ shown in an X-ray analysis was the main Na-O-Te containing compound. So, a modified reaction can be offered for this process:

$$4Cu_2Te + Na_2CO_3 + 7O_2 = 8CuO + Na_2Te_2O_2 + CO_2^*$$
 (Eq. 5.11)

The presence of silica in the soda slag introduces another series of reactions to the system:

$$Na_2CO_3 = Na_2O + CO_2$$
 $\Delta G_{1200C} = -338581.6 \ J/mole$ (Eq. 5.12) $Na_2O + 2SiO_2 = Na_2O*2SiO_2$ $\Delta G_{1200C} = -254866.7 \ J/mole$ (Eq. 5.13) $Na_2O + SiO_2 = Na_2O*SiO_2$ $\Delta G_{1200C} = -233756.3 \ J/mole$ (Eq. 5.14)

Sodium carbonate reacts with silica thereby reducing the activity of Na_2O in the system. This eventually decreases the amount of tellurium recovered to the slag phase, as shown by the experimental data shown in Figure 5.8 b.

• No thermodynamic data were found in a database for the compounds Na₂TeO₃ or Na₂Te₄O₉.

It can be concluded that

- It is not possible to keep Rh in dore metal when the Po2 of the gas phase exceeds 10⁻⁴. But if dore metal is slowly cooled before oxygen treatment it is possible to get slags enriched with Rh and not lose metal with the outgoing gases.
- 2. For current practice, the best Te elimination can be achieved with higher Na₂O activity in the slag.
- 3. To improve tellurium elimination from the dore metal in a form of intermetallic (Na₂Te) metallic Na can be added to the alloy.

Cu and Pb

The amount of Cu and Pb in the dore metal decreased as a result of chemical reaction with the slag and gas phase. This leads to an increased presence of these metals in the slag as oxides and silicates. The chemistry of the recovery of these two metals can be described with the equations below (solubility of Pb and Cu in Ag is very low, presence of the other soluble impurities possibly making it close to zero, because of that a_{Cu} and a_{Pb} considered to be 1, $P_{O_2} = 1$ atm):

$$Pb + 0.5O_2 = PbO$$
 $\Delta G_{1200C} = -130127 \ Jmole$ (Eq. 5.15)

$$Pb+0.50_2+2Si0_2=Pb0*2Si0_2$$
 $\Delta G_{12000c}=-458619.6$ Jmole (Eq. 5.16)

$$Pb + 0.5O_2 + SiO_2 = PbO^*SiO_2$$
 $\Delta G_{1200*C} = -35850.1 \text{ J/mole}$ (Eq. 5.17)

$$Cu+0.5O_2=Cu_2O$$
 $\Delta G_{12wec}=-62189$ J/mole (Eq. 5.18)

Copper also has a tendency to form Cu_2TeO_6 , according to equation:

$$Cu_2O + TeO_2 = Cu_2TeO_3^*$$
 (Eq. 5.19)

• ΔG_{1200℃} for reaction 5.19 could not be calculated; data are not present in the database.

Copper and lead behaved similarly depending on P_{O_2} and the SiO₂ content of the soda slag. According to Figure 5.5b increasing the silica content in slag led to an increased copper content in slag. The same effect was observed when the P_{O_2} was increased, which corresponds to the chemistry of the recovery process. For Cu and Pb increasing P_{O_2} from 10⁻⁸ to 10⁻⁴ decreased the content of both impurities in the dore metal: from 275 ppm to 42 ppm for Pb and from 1.6 to 0.89 % for Cu.

It can be concluded that:

1. It is not necessary to increase the P_{o_2} in a system to more than 10^{-2} atm to reduce the Pb content in a dore metal to 100 ppm.

2. Increasing P_{o_2} in the system together with increasing silica content in slag increases the possibility to reduce Cu content in dore metal.
5.3 Slag chemistry

5.3.1. Soda slag decomposition during the experiments

Figure 5.9 shows the amount of carbon remaining in the soda slag after the experiments (Table 4.2.), i.e the extent of decomposition degree of sodium carbonate. The dependence on P_{O_2} of the gas phase and SiO₂ in the soda slag is also shown. These graphs show that P_{O_2} of the gas phase in the range studied does not influence the decomposition of sodium carbonate, whereas increasing SiO₂ content in the slag increased sodium carbonate decomposition.

Figure 5.9. Decomposition of sodium carbonate as a function of P_{O_2} of the gas phase and SiO_2 content in soda slag.

1- 0% SiO₂ in soda slags, SDM
 2- 5% SiO₂ in soda slags, SDM
 3-10% SiO₂ in soda slags, SDM
 4- 0% SiO₂ in soda slags, CDM



The data shown in Figure 5.9 may be used to calculate the degree of decomposition of sodium carbonate for different conditions, Table 5.3. From Figure 5.9 it can also be seen that the amount of carbon left in soda slag after reaction with CDM has an average value around 5.5 wt %. This fact means that the amount of silica introduced to the system by the CDM was in a range of 8-10 wt %.

These results correspond to the results of investigation reported by T. Yokokawa and M. Shinmei on the thermodynamic stability of sodium carbonate (62). They conclude that with the basicity of slag higher than 2.5 and $\log P_{O_2} >$ -8, sodium carbonate has a tendency to decompose to Na₂O and CO₂, with Na₂O reacting with SiO₂. They defined basisity as pO= - log **a**_{Na2O}, where the activity was referred to pure Na₂O

Table 5.4Decomposition degree of sodium carbonate as a function of percent SiO_2 in
soda slag.

No.	SiO ₂ in soda slag, %	Average C left in soda slag, %	Decomposed sodium carbonate, %
1	0	8	29.2
2	5	6.5	42.48
3	10	5	55.75

5.3.2 Influence of Po, and SiO, on impurity content of soda slag

Au, Pt and Pd.

The presence of SiO_2 in slag did not influence the distribution coefficients of Au, Pt and Pd, Figures 5.1-5.3. But in a real industrial process with vessel rotation, increased noble metal loss with increasing SiO_2 content in slag is to be expected because of the increased viscosity of slag. All slag samples had numerous fine particles of metallic phase when examined under the microscope (Experiment 7, SEM) prior to their being ground, Figure 5.1.

This observation may be explained by the increase in the slag viscosity. Riabco et.

al. developed a method for determining in which form the noble metals loss occurs in industrial slags. Their conclusion was that all the platinum group metals are present is slags in the form of mechanical loss. In order to decrease the amount of these metals in slags it is necessary to increase the settling time for the slag, increase process temperature and increase the amount of silica in slags of slag-cleaning and ore-smelting furnaces (23). The same conclusions can be made to decrease the loss of Au, Pt and Pd in soda slag.



Figure 5.10 Particles of the metallic phase, light phase, in soda slag prior to being ground.

As shown in Table 5.4, the ΔG of reaction in the silver - soda slag - gas phase system becomes more negative with increasing P_{O_2} . However, according to the calculations introduced in the section on Metal Chemistry, it not possible for Pt, Au and Pd to react with oxygen under the present experimental conditions. Thus, it is possible to lose some Ag as oxide or in the form of intermetallics, but Au and Pt are always in the form of mechanical loss. Figures 5.11 - 5.12 show how the amount of silver in soda slag depends on P_{o_2} of the gas phase and the resulting ΔG of interaction between silver, soda slag and the gas phase as calculated by the *EQUILIB* subroutine of the F*A*C*T, assuming that activity of silver, a_{A_B} , is equal to 1 (the amount of Ag in an alloy 94%) and temperature of the interaction 1200°C.

Table 5.5 ΔG of reaction in Ag - soda slag - gas phase system, calculated by theEQUILIB subroutine of the F*A*C*T.

No.	Partial pressure of oxygen in gas phase, Po ₂	ΔG of reaction
1	1.0E-8ATM	-901544.4
2	1.0E-6ATM	-912960.5
3	1.0E-4ATM	-924376.6
4	1.0E-2ATM	-941500.7
5	2.1E-1ATM	-943340.0
6	1.0 ATM	-947208.8

Se, Te and Rh

The influence of SiO_2 in the soda slag on Te, Se, Rh can be seen only for P_{O_2} of the gas phase equal to 10^{-8} atm. Increasing SiO_2 from 0 to 10% increased metal content in the soda slag from 1.5 to 10 times. When the oxygen content in the gas phase was low, silica was able to reduce the recovery of Te, Se and Rh from dore metal.

Se, Te

Experiments showed that the amount of Se in soda slags on top of the SDM remained practically constant with increasing P_{O_2} of the gas phase. This corresponds to the results for other types of slags (82,83). Nagamori (82) found that Se in iron silicate slags for steel production is present in both forms: elemental and iron metallide. Those forms of dissolution of Se in slag result in an increased solubility at lower values of P_{O_2} with near constant values at higher P_{O_2} .

Silica addition to the slag phase decreased selenium holdup in the soda slag, because reaction between sodium oxide and silica is preferred. According to (62), the presence of silica in a system decreases oxygen pressure in the slag phase.

As was observed in the SEM analysis, selenium in soda slags was present mainly in phases containing sodium, Table 4.7, possibly Na₂SeO₃. The results of the experimental work and SEM analysis showed that silica present in the soda slag may work as a barrier for selenium removal from the slag when $P_{O_2} = 10^{-8}$ atm. The SEM analysis also showed that the amount of selenium-containing phases below the slag separation layer was higher than in the upper part of the slag. This was because Te and Se oxides are volatile and even if selenium was present in slag as an intermetallic impurity (for example Ag₂Se), it will be recovered from the slag to the gas phase with increasing P_{O_2} .

The amount of Te present in the slag increased with increasing P_{O_2} , Figure 5. b. This observation corresponds to the chemistry of slag-tellurium interaction discussed in "Metal Chemistry" (Chapter 5.2.4).

According to the data presented in Table 5.5, the possibility of tellurium - slag - gas phase interaction increased with P_{O_2} in the gas phase, but the possibility of this reaction is higher with 5% of SiO₂ than with 10% of SiO₂ in slag. For 5% silica in slag, the diffusion of oxygen to the metal through the slag is easier and at the same time more Na₂O is left to react with Te or TeO₂. Increasing silica in slag possibly suppressed the diffusion of oxygen through the slag and it reacted with Na₂O decreasing the activity of this component in slag. Higher contents of Te in soda slag for the CDM (Figure 5.8 b) occurred because of the presence of the dark film containing impurities on top of CDM before treatment. The results of calculations, Table 5.5, show that with increasing P_{o_2} the ΔG of reaction between Te - soda slag and gas phase becomes more negative (see Appendix III).

No.	Po ₂ , atm	ΔG of reaction, 5% SiO ₂	ΔG of reaction, 10% SiO ₂
1	1.0E-8ATM	-806959.3	-801989.2
2	1.0E-6ATM	-	-817006.9
3	1.0E-4ATM	-829791.5	-828423.0
4	1.0E-2ATM	-846915.6	-845547.2
5	2.1E-2ATM	•	-847386.4
6	1.0 ATM	-852623.7	-851255.2

Table 5.6 Calculated data for the ΔG of Te reaction with soda slag and the gas phase.

Rh:

Increasing P_{O_2} increased Rh content in the soda slag, possibly because the easily volatile oxide, RhO₂, leaves the metal, and tries to penetrate through the slag. Increasing P_{O_2} increases the oxide activities in the slag. This may increase the chance of chemical reaction between RhO₂, TeO₂ and other oxides so that Rh₂ (Fe,Cu, Ni)TeO₆ may be produced. Tied as a compound with the other oxides, Rh may tend to stay in the slag and not evaporate.

Following the results of the SEM analysis of soda slag and the dark film on the dore metal, where Rh was found in the phase where Ni was also present, it can be concluded that Rh was possibly present in the dore metal in the form of Rh-Ni intermetallic.

No.	Po2	ΔG of reaction, 5% SiO ₂	ΔG of reaction, 10% SiO ₂
1	1.0E-8ATM	-804508.2	-801989.2
2	1.0E-6ATM	-	-
3	1.0E-4ATM	-827340.4	-
4	1.0E-2ATM	-844464.5	-
5	2.1E-2ATM	-	-
6	1.0 ATM	-850172.5	-847653.5

Table 5.7Results of the calculations for rhodium - soda slag - gas phase interaction.
(see Appendix III for details)

Their is a rough correspondence between the influence of silica on the rhodium content of the slag and influence of silica on the Gibbs energy of reaction (Appendix III).

Cu, Pb

The presence of Cu in soda slags is of practical and theoretical interest. Copper may be present in slags as intermetallic particles insoluble in dore metal and transported to the slag with gas bubbles as well as being dissolved in the slag. As was found by (75), at oxygen saturation and in contact with pure copper, the solubility of Cu in sodium carbonate slag is only 0.85%. The results of the chemical analysis for the study were presented in Table 4.2.

The SEM analysis shows that copper was present in most of the slag phases and all these phases also had silicon and/or tellurium in them. According to the results of CANMET research (84) and SEM analysis of dore metal before treatment, copper leaves dore metal in the form of an insoluble intermetallic - Cu_2Te or Cu_2O . It has been reported (85) that sintering tellurides of Cu, Ag and Au with sodium carbonate produces sodium tellurate. High temperature sintering of Te O₂ with PbO₂ also forms the corresponding tellurates (86, 87). Thus Cu may be present in soda slags in the form of tellurates or silicates and much of it can be found as intermetallics in the slag separation layer, Figures 4.8 - 4.11, Table 4.7. Lead was also always present in phases containing silicon and tellurium as lead silicates or tellurates.

No.	Partial pressure of oxygen in a gas phase, Po ₂	ΔG of reaction
1	1.0E-8ATM	-802392.9
2	1.0E-6ATM	-813809.0
3	1.0E-4ATM	-825225.1
4	1.0E-2ATM	-842349.2
5	2.1E-2ATM	-844188.4
6	1.0 ATM	-842349.2

Table 5.8 Results of calculations for the lead - soda slag - gas phase system.

Copper and lead in soda slags had very similar behaviour depending on P_{o_2} or SiO₂ presence in the soda slag, Figures 5.4 - 5.5. According to these graphs, increasing silica in slag led to an increase in the copper content of the slag, (the same effect as increasing P_{o_2}). Higher amounts of lead in the CDM tests were a result of the dark film present on the metal surface before treatment. The ΔG of reaction between lead - soda slag - gas phase were calculated by the EQUILIB subroutine of the F*A*C*T, Table 5.7

Table 5.7 shows that the ΔG of reaction has a negative sign, so the reaction will go to the right. Detailed calculations are presented in Appendix III.

5.3.1 Slag separation.

The presence of a black separation layer between two slag layers was mentioned as an unexpected result of the experimental work. In each experiment the position of the intermetallic layer and thus the sizes of the slag layers varied. These differences are the result of the chemistry of the system, controlled by oxygen activity in the slag and metal phases.

The SEM analysis shows that the black separation layer consisted of intermetallic phases (Table 4.7 and Figures 4.8-4.11). The nature of the intermetallic phases in a layer corresponded to the nature of the inclusions found by SEM analysis in dore metal before and after the treatment. Hexagonal particles containing Rh were found in this layer. In the SEM image, the slag layers had a similar appearance, but part of the soda slag closest to the metal contained more linear and curvilinear particles containing Se, than the upper part of the slag.

To clarify the nature of the black separation layer in the slag phase, fast cooling experiments were performed. It was found that the slags of the fast cooling experiments did not have a black slag separation layer.

This phenomenon can be explained from the point of view of the structural changes that occurred in the system during the melting and cooling period. The results of the slag melting experiments showed that the melting process of the slag occurred in a stepwise manner over a temperature range from 690°C to 1100°C. Crystallization of the slag phases during freezing also followed this pattern.

Partial slag crystallization led to a sponge-type structure. For most of the soda slag samples (Table 3.2.1) this process started when the temperature dropped below 1040°C. The temperature of the dore metal solidification is approximately 960°C, and some insoluble species (like Rh, Pb, Cu, Te) float on the surface of the melt. Species which exhibited decreased solubility at lower temperature possibly came out of the melt during the temperature drop and the crystallization of the dore metal. These species formed a film which was then absorbed by slag.

It can be concluded that:

- 1. The decomposition degree of sodium carbonate increases with increase of silica in soda slag.
- 2. Increase of silica content in slag may increase precious metal loss in slag in the form of metallic drops if the system is mixing during the process.
- 3. Increase of silica content in soda slag at low values of P_{o_2} decreases Te and Se removal from dore metal.
- Rhodium was found to be present in soda slag in Te-based phase containing Ni. Thus, Rh loss with soda slag is of a chemical nature, unlike Au, Pt and Pd.
- Increasing silica content in soda slag noticeably increases the Pb and Cu removal from dore metal especially at low Po2.
- 6. Separation of slag during the slow cooling experiments with the intermetallic layer can be used in a slag cleaning process.

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CHAPTER 6. CONCLUSIONS

- 1. The distribution coefficient, $L_{Me}^{Dm/SS}$, of Rh, Se and Te between dore metal and soda slag for synthetic dore metal (SDM) markedly decreased (100 times) with increasing P_{O_2} from 10⁻³ to 10⁻⁶. Further increase in P_{O_2} did not significantly influence the $L_{Me}^{Dm/SS}$ of these metals at 1200°C, and the resulting values of $L_{Me}^{Dm/SS}$ are much lower than unity. It was concluded that these impurities were almost completely removed. For commercial dore metal (CDM), however, the $L_{Rh}^{Dm/SS}$ did not change so significantly (3.5 times). The difference in behaviour of SDM and CDM was attributed to differences in the compounds containing these elements in CDM and SDM.
- 2. The distribution coefficients of Cu and Pb had a tendency to decrease strongly when P₀₂ was increased from 10⁻⁴ to 10⁻⁴ and then remained constant with further increase in P₀₂. Increasing P₀₂ from 10⁻⁴ to 10⁻⁴ decreased the content of both impurities in the dore metal: from 275 ppm to 42 ppm for Pb and from 1.6 % to 0.89 % for Cu. It was concluded that it is not necessary to clean the dore metal from lead down to100 ppm during the earlier steps of the TBRC process because even with P₀₂ of the gas phase at 10⁻² atm, the amount of lead left was found to be lower than 100 ppm in most experiments.
- 3. Increasing silica in soda slag
 - a) increases the extend of decomposition of sodium carbonate
 - b) decreases Te and Se removal from dore metal at low values of $P_{o_{n}}$.
 - c) increases the Pb and Cu recovery from dore metal noticeably at low P_{o_n} .
- 4. Better separation of slag from the melt occurred with an increase in the amount of silica in the slag. But at the same time, the increased silica content in soda slag may increase the losses of dore metal the form of mechanical inclusions if the system is subjected to mixing during the process. To avoid losses of Au, Pt and Pd in the soda slag, it is necessary to increase the time for the system to settle down.

Chapter 6. Conclusions

- 5. The dark film on commercial dore metal is a result of the solidification process of the dore metal and consisted of intermetallic and slag particles precipitated from the dore metal during solidification. The presence of this film could possibly be used during the commercial process as an indicator of impurity removal.
- 6. Formation of the black intermetallic layer between two layers in soda slag was a result of slow solidification. It can be concluded that skiming of slag would be more effective after a longer standing of dore metal - soda slag system without agitating. This will increase the amount of the intermetallic phases removed by slag.
- 7. At the same time, separation of slag during the slow cooling experiments with the intermetallic layer may be used for the slag cleaning process.
- Rhodium does not remain in dore metal when the P₀₂ of the gas phase exceeds 10⁻⁴.
 But if dore metal is slowly cooled before oxygen treatment it is possible to get slags enriched with Rh and not lose metal with the outgoing gases.
- Rhodium was found to be present in soda slag in a tellurium-based phase containing Ni. It was concluded that Rh loss with soda slag is of a chemical nature, which differentiates it from Au, Pt, and Pd.
- 10. For current practice the best Te elimination can be achieved with higher Na₂O activity in the slag. To improve tellurium elimination from the dore metal (in the form of intermetallic (Na₂Te)) metallic Na could be added to the alloy.
- 11. The chemical interaction of magnesia crucibles with the system soda slag dore metal was determined. Also SEM analysis of soda slag and dore metal (before and after the soda slag treatment) was carried out for the first time. Chemical and mineralogical results are presented in the thesis.

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<u>A P P E N D I X</u>

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0.90Na2CO3+0.10SiO2+O2+0.015Te+ (298.15K,1ATM,S1) (298.15K,1ATM,S1) (298.15K,1ATM,G) (298.15K,1ATM,S1) Ar = (298.15K,1ATM,G) 2.1685 mol (0.46115 Ar + 0.45444 02 CO₂ + 0.80419E-01 + 0.36359E-02 TeO2 TeO + 0.33611E-03 + 0.16974E-04 Na + 0.40731E-05 Te2O2 + 0.31118E-05 NaO + 0.18689E-05 0 + 0.17644E-05 Te CO + 0.39024E-06 + 0.18477E-07 Te₂ 03 + 0.70719E-09 Т Te204 + 0.83563E-10 + 0.11343E-10 Na2 + 0.82403moi (0.88056 Na2CO3 Т + 0.79960E-01 (Na2O)2(SiO2)(Na2O)(SiO2) Т + 0.21461E-01 + 0.99664E-02 Na6Si2O7 Т + 0.76464E-02 TeO₂ Т + 0.32336E-03 Na2O Т + 0.77809E-04 Te Т + 0.22682E-05 Na + 0.87726E-06 SiO2 Т + 0.27142E-06 (Na2O)(SiO2)2 + 0.26155E-07 Na2Te + 0.31749E-14 NaTe3 ********* ***** DELTA H DELTA G DELTA V DELTA S DELTA U DELTA A REACT V (1) (J) (J) (J/K) **(J) (l) (J**) -S1---S1---G1----G1----296614.6 -851255.2 0.213E+03 388.792 275014.2 -872855.6 0.489E+02

Calculations performed by the EQUILIB subroutine of the F*A*C*T

============================== last line

(298.15K,1ATM,S1) (298.15K,1ATM,S1) (298.15K,0.1ATM,G) (298.15K,1ATM,Si) Ar =

(298.15K,1ATM,G)

2.1685	mol (0.46115 + 0.45444 + 0.80419E-01 + 0.36359E-02 + 0.33611E-03 + 0.16974E-04 + 0.40731E-05 + 0.31118E-05 + 0.18689E-05 + 0.17644E-05 + 0.39024E-06	Ar O2 CO2 TeO2 TeO Na Te2O2 NaO O Te CO		
	+ 0.18477E-07 + 0.70719E-09	1e2 O3		
	+ 0.83563E-10	Te2O4	Т	
	+ 0.11343E-10	Na2		
	+ 0.15113E-20 + 0.44833E-21	SIU Tes	т	
	+ 0.29530E-27	CTe	T)	
	(1473.00 K, 1.	0000 atm, gas)	-/	
+ 0.82403	mol (0.88056	Na2CO3	-	
	+ 0.79960E-01	(Na2O)2(SiO2)	T	
	+ 0.21461E-01	(Na2O)(SiO2)	1	
	+ 0.99664E-02	Na6Si2O7	_1.	
	+ 0.76464E-02	TeO2	1	
	+ 0.32336E-03	Na2O	-	
	+ 0.77809E-04	Te	T	
	+ 0.22682E-05	Na	Т	
	+ 0.87726E-06	SIU2		
	+ 0.271421-06	(Na2O)(SiO2)2	1	
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*******	*****	*******	*******	*******
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(298.15K,1ATM,S1) (298.15K,1ATM,S1) (298.15K,**0.21ATM**,G) (298.15K,1ATM,S1) Ar =

(298.15K,1ATM,G)

- 3.

2.1685	mol	(0.46115		Ar						
	+	0.45444		02						
	+	0.80419E-0)1	CO2						
	+	0.36359E-0	2	TeO2						
	+	0.33611E-0	13	TeO						
	+	0.16974E-0	14	Na						
	+	0.40731E-0	15	Te2O2						
	+	0.31118E-0)5	NaO						
	÷	0.18689E-0	15	0						
	÷	0.17644E-0	15	Te						
	+	0.39024E-0	6	CO						
	+	0.18477E-0)7	Te2						
	+	0.70719E-0	19	O3						
	+	0.83563E-1	0	Te2O4			Т			
	+	0.11343E-1	0	Na2						
	+	0.15113E-2	0	SiO		_				
	+	0.44833E-2	1	Tes		T				
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	+	0.75004E-0	12	TeO2			r			
	+	0.70404E	13	Na20			•			
	+	0.77809E-(4	Te		Т				
	+	0.22682E-()5	Na		- т	•			
	+	0.87726E-0	6	SiO2		-				
	+	0.27142E-(6	(Na2O)	(SiO2)2		Т			
	+	0.26155E-0)7	Na2Te			-			
	+	0.31749E-1	4	NaTe3						
*******	*****	********	****	******	******	*****	****	*********	*****	
DELTA H	DE	LTA G D	ELT.	AV I	DELTA S	DELTA	U	DELTA A	REACT V	
(J)		(J)		(l)		(J/K)		(J)	ወ	(1)
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(298.15K, 1ATM, S1) (298.15K, 1ATM, S1) (298.15K, 1.0E-4ATM, G) (298.15K, 1ATM, S1) Ar =

(298.15K,1ATM,G)

2.1685	mol	(0.46115	Ar					
	+	0.45444	O2					
	+	0.80419E-01	CO2					
	+	0.36359E-02	TeO2					
	+	0.33611E-03	TeO					
	+	0.16974E-04	Na					
	+	0.40731E-05	Te2O2					
	+	0.31118E-05	NaO					
	+	0.18689E-05	0					
	+	0.17644E-05	Te					
	+	0.39024E-06	CO					
	÷	0.18477E-07	Te2					
	+	0.70719E-09	03					
	+	0.83563E-10	Te204		Т			
	+	0.11343E-10	Na2					
	+	0.15113E-20	210		~			
	+	0.44833E-21			T			
	+	0.29530E-27			1)			
		(14/3.00 K, I.	0000 at	m, gas)				
+ 0.82403	mo	1 (0.88056	N270	ากง				
1 0.02405		0 79960 -01	(Na2O)	2(5)02)	т			
	+	0.21461E-01	(Na2O)	(SiO2)	т			
	+	0 99664E-02	Na6Si2	07	т			
	+	0.76464E-02	TeO2	0,	т			
	+	0.32336E-03	Na2O		-			
	+	0.77809E-04	Te		Т			
	+	0.22682E-05	Na		T			
	+	0.87726E-06	SiO2					
	+	0.27142E-06	(Na2O)	(SiO2)2	Т	•		
	+	0.26155E-07	Na2Te					
	+	0.31749E-14	NaTe3					
		(1473.00 K,	1.0000	atm, liquid)				
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(298.15K,1ATM,S1) (298.15K,1ATM,S1) (298.15K,1.0E-6ATM,G) (298.15K,1ATM,Si) Ar =

(298.15K,1ATM,G)

2.1685	mol	(0.46115		Ar					
	÷	0.45444	(D 2					
	+	0.80419E-()1	CO2					
	+	0.36359E-()2	TeO2					
	+	0.33611E-0)3	TeO					
	+	0.16974E-0)4	Na					
	+	0.40731E-()5	Te2O2	2				
	+	0.31118E-()5	NaO					
	÷	0.18689E-()5	0					
	+	0.17644E-()5	Te					
	+	0.39024E-0)6	CO					
	+	0.18477E-0)7	Te2					
	+	0.70719E-0)9	O3					
	+	0.83563E-1	10	Te2O4	ŧ.		Т		
	+	0.11343E-1	10	Na2					
	+	0.15113E-2	20	SiO					
	+	0.44833E-2	21	Te5			Т		
	÷	0.29530E-2	27	CTe			T)		
	((1473.00 K	, 1.00	00 a	ıtm, gas)				
+ 0.82403	mol	(0.8805	6	Na2	CO3				
	+	0.79960E-0)1	(Na2O))2(SiO2)		Т		
	+	0.21461E-0)]	(Na2O)(SiO2)		Т		
	+	0.99664E-0)2	Na6Si	207		Т		
	+	0.76464E-0)2	TeO2			Т		
	+	0.32336E-0)3	Na2O					
	+	0.77809E-0)4	Te			T		
	+	0.22682E-0)5	Na			Т		
	+	0.87726E-()6	SiO2					
	+	0.27142E-()6	(Na2C))(SiO2)2		Т		
	+	0.26155E-0)7	Na2Te	;				
	+	0.31749E-1	4	NaTe3	5				
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(298.15K, 1ATM, S1) (298.15K, 1ATM, S1) (298.15K, 1.0E-8ATM, G) (298.15K, 1ATM, S1) Ar =

(298.15K,1ATM,G)

+ 0.45444 O2	
+ 0.80419E-01 CO2	
+ 0.36359E-02 TeO2	
+ 0.33611E-03 TeO	
+ 0.16974E-04 Na	
+ 0.40731E-05 Te2O2	
+ 0.31118E-05 NaO	
+ 0.18689E-05 O	
+ 0.17644E-05 Te	
+ 0.39024E-06 CO	
+ 0.18477E-07 Te2	
+ 0.70719E-09 O3	
+ 0.83563E-10 Te2O4 T	
+ 0.11343E-10 Na2	
+ 0.15113E-20 SiO	
+ 0.44833E-21 Te5 T	
+ 0.29530E-27 CTe T)	
(1473.00 K, 1.0000 atm, gas)	
+ 0.82403 mol (0.88056 Na2CC3)	
+ 0.79960E-01 (Na2O)2(SiO2) T	
+ 0.21461E-01 (Na2O)(SiO2) T	
+ 0.99664E-02 Na6Si2O7 T	
+ 0.76464E-02 TeO2 T	
+ 0.32336E-03 Na2O	
+ 0.77809E-04 Te T	
+ 0.22682E-05 Na T	
+ 0.87726E-06 SiO2	
+ 0.27142E-06 (Na2O)(SiO2)2 T	
+ 0.26;55E-07 Na2Te	
+ 0.31749E-14 NaTe3	

DELTA H DELTA C DELTA V DELTA S DELTA LI DEL HA A REACT V	
$(I) \qquad (I) \qquad (I) \qquad (IV) \qquad (IV) \qquad (I) \qquad (IV) \qquad (IV)$	ሐ
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296614.6 -805590.9 -0.245E+10 235.633 275014.2 -827191.3 0.245E+10	

Ar (298.15K.1A	TM.G	=)						
2.1746	mol	(0.45986	Ar					
	+	0.45984	CO2					
	+	0.802546-01	DF0					
	- -	0.234336-04	N ₂	1 2				
	+ -	0.170072-04	NaO	•				
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	, +	0.11387E-10	Na2					
	- -	0 14875F-20	SiO					
	+	0.45887E-24	Rh		T			
	. ((1473.00 K, 1.	.0000	atm, gas)	-)			
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	- -	0.007372-01	(Na2 (Na2	(0)2(3)02)	1 T			
	- -	0.214562-01	No69	Si207	L T			
	+ -	0.326555-03	No71	0	1			
	, +	0.320332-05	Na	0	т			
	+	0.86860E-06	SiO2	,	•			
		0.26871E-06	(Na2	- 20)(SiO2)2	т	•		
	+	0.25823E-12	Rh		-			
	+	0.13239E-28	Si					
	. ((1473.00 K, 1.	.0000	atm, liquid)				
	÷	0.00000	ni Na2(°03				
	Ŧ	1473.00 K 1	0000	atm S3 a≡0	42661			
		(1475.00 K, 1.		aun, 55, a—0	.42001)			
*********	*****	******	******	******	******	******	*****	
DELTA H	DE	LTA G DEL	TAV	DELTA S	DELTA U	DELTA A	REACT V	-
(1)		(J)	(1)	(J/K)	}	(J)	(1)	(l
*********	*****	******	******	********	********	*********	*****	
-2121G	i51							

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0.90Na2CO3	3+0.10SiO2+O2+0.00	00051Rh+ FM S1) (208 15K 1)	ATM (C) (208	158 1ATM 9	21)	
(290.15K,17	=	(290.1JK,1/	ATMI,O) (290	. 156, 17 1 101, 2	,	
(298.15K,1A	TM,G)					
2.1746	mol (0.45986	Ar				
	+ 0.45984	O2				
	+ 0.80254E-01	CO2				
	+ 0.23453E-04	RhO2				
	+ 0.17007E-04	Na				
	+ 0.31363E-05	NaO				
	+ 0.18799E-05	0				
	+ 0.38714E-06	CO				
	+ 0.71984E-09	O3				
	+ 0.11387E-10	Na2				
	+ 0.14875E-20	SiO				
	+ 0.46887E-24	Rh	T)			
	(1473.00 K, 1.0	000 atm. gas)				
+ 0.81752	mol (0.88741	Na2CO3				
	+ 0.80737E-01	(Na2O)2(SiO2)	Т			
	+ 0.21458E-01	(Na2O)(SiO2)	Т			
	+ 0.10062E-01	Na6Si2O7	Т			
	+ 0.32655E-03	Na2O				
	+ 0.22727E-05	Na	Т			
	+ 0.86860E-06	SiO2				
	+ 0.26871E-06	(Na2O)(SiO2)2	Т			
	+ 0.25823E-12	Rh				
	+ 0.13239E-28	Si)				
	(1473.00 K, 1.0	000 atm, liquid)				
	+ 0.00000 mo	l Na2CO3				
******	******	*****	******	******	*****	
DELTA H	I DELTA G DELT	A V DELTA S	DELTA U	DELTA A	REACT V	
(L)	(L)	(l) (J/K	()	(J)	(J)	(1)
*******	nje dan ang ang ang ang ang ang ang ang ang a	*****	******	*****	****	
-S1S1G	ISIGI					
298268.1	-847653.5 0.214E+03	388.060 27659	3.4 -869328.	2 0.489E+0	2	
======	=======================================			= = last line		
======	.===============			= =		



\r	=
298.15K.1A	NTM.G)
2.0934	mol (0.47768 Ar
	+ 0.47766 O2
	+ 0.44600E-01 CO2
	+ 0.24362E-04 RhO2
	+ 0.23329E-04 Na
	+ 0.43849E-05 NaO
	+ 0.19160E-05 O
	+ 0.21109E-06 CO
	+ 0.76210E-09 O3
	+ 0.21428E-10 Na2
	+ 0.22388E-21 SiO
	+ 0.46887E-24 Rh T)
	(1473.00 K, 1.0000 atm, gas)
0.90569	mul (0.94583 Na2CO3
	+ 0.45553E-01 (Na2O)2(SiO2) T
	+ 0.63127E-02 (Na2O)(SiO2) T
	+ 0.16702E-02 Na6Si2O7 T
	+ 0.62628E-03 Na2O
	+ 0.31176E-05 Na T
	+ 0.13324E-06 SiO2
	+ 0.12126E-07 (Na2O)(SiO2)2 T
	+ 0.25823E-12 Rh
	+ 0.19549E-29 Si)
	(1473.00 K, 1.0000 atm, liquid)
	+ 0.00000 mol Na2CO3
	(1473.00 K, 1.0000 atm, S3, a=0.45470)

DELTA H	I DELTA G DELTA V DELTA S DELTA U DELTA A REACT V
(J)	(J) (l) (J/K) (J) (J)
*********	**************************************
S!S1G	1S1G1
297622.5	\$50172.6 0.204E+03 385.450 276941.5 -870853.5 0.489E+02

•

2.0934	mol ((0.47768	Ar					
	+ 0.4	47766	02					
	+ 0.4	14600E-01	CO2	`				
	+ 0.	24362E-04	RhO	2				
	+ 0	23329E-04	Na N-O					
	+ 0.4	43849E-05	Nau)				
	+ U.							
	+ 0.2	21109E-00						
	+ 0. → 01	1429E 10	05					
	± 0.2	214205-10	SiO					
	+ 0	122300E-21 122300E-21	210		T	`		
	- + 0.4	10007E-24	0.000	atm gac)	1)		
	、 - ·			Bus)				
0.90569	mol (0.94583	N	a2CO3				
	+ 0.	45553E-01	(Na	20)2(SiO2)		т		
	+ 0.0	63127E-02	(Na	2O)(SiO2)		Ť		
	+ 0.	16702E-02	Na6	Si2O7		T		
	+ 0.0	62628E-03	Na2	0				
	+ 0.	31176E-05	Na		Т			
	+ 0.	13324E-06	SiO	2				
	+ 0.	12126E-07	(Na	2O)(SiO2)2		Т		
	+ 0.3	25823E-12	Rh					
	+ 0.	19549E-29	Si)					
	(14	73.00 K. 1	0000	atm, liquid)			
	+ 0.9	00000 m	ol Na2	CO3				
	(14	73.00 K, 1	.0000	atm, S3, a	=0.45470)		
*****	*******	*********	******	*******	********	****	*********	*****
DELTA H	I DELT	A G DEL	TA V	DELTA S	DELTA	U	DELTA A	REACT V
(J)		(J)	(l)		(J/K)		(J)	(J)
0.95Na2CO3	+0.055iO2+O2+0.000051Rh+ (TM_S1) (298.15K, LATM,S1) (298.15K, L0E-4ATM,G) (298.15K, LATM,S1)							
-------------	---							
Ar	=							
(298.15K,1A	TM,G)							
2.0934	mol (0.47768 Ar							
	+ 0.47766 O2							
	+ 0.44600E-01 CO2							
	+ 0.24362E-04 RhO2							
	+ 0.23329E-04 Na							
	+ 0.43849E-05 NaO							
	+ 0.19160E-05 O							
	+ 0.21109E-06 CO							
	+ 0.76210E-09 O3							
	+ 0.21428E-10 Na2							
	+ 0.22388E-21 SiO							
	+ 0.46887E-24 Rh T)							
	(1473.00 K, 1.0000 atm, gas)							
+ 0.90569	mol (0.94583 Na2CO3							
	+ 0.45553E-01 (Na2O)2(SiO2) T							
	+ 0.63127E-02 (Na2O)(SiO2) T							
	+ 0.16702E-02 Na6Si2O7 T							
	+ 0.62628E-03 Na2O							
	+ 0.31176E-05 Na T							
	+ 0.13324E-06 SiO2							
	+ 0.12126E-07 (Na2O)(SiO2)2 T							
	+ 0.25823E-12 Rh							
	+ 0.19549E-29 Si)							
	(1473.00 K, 1.0000 atm, liquid)							
	+ 0.00000 mol Na2CO3							
	(1473.00 K, 1.0000 atm, S3, a=0.45470)							
DELTAN								
	DELIAG DELIAV DELIAS DELIAU DELIAA KEACIV							
(1)	(J) (J) (J/K) (J) (J) (I)							
********	*************							
-S1S1G1	S1G1							
297622.5 -	827340.4 -0.244E+06 308.871 276941.5 -848021.4 0.245E+06							
=====	======================================							

0.95Na2CO3 (298.15K,17	3+0.05SiO2+O2+0.00 ATM,S1) (298.15K,1AT	10051Rh+ (M,S1) (298,15K,1	0E-8ATM.G) (29	98.15K.1ATM.S	(1)
Ar	=			·····	-,
(298.15K,1A	.TM.G)				
2.0934	mol (0.47768	Ar			
	+ 0.47766	02			
	+ 0.44600E-01	CO2			
	+ 0.24362E-04	RhO2			
	+ 0.23329E-04	Na			
	+ 0.43849E-05	NaO			
	+ 0.19160E-05	0			
	+ 0.21109E-06	CO			
	+ 0.76210E-09	O3			
	+ 0.21428E-10	Na2			
	+ 0.22388E-21	SiO			
	+ 0.46887E-24	Rh	T)		
	(1473.00 K, 1.0	000 atm, gas)	·		
+ 0.90569	mol (0.94583	Na2CO3			
	+ 0.45553E-01	(Na2O)2(SiO2)	Т		
	+ 0.63127E-02	(Na2O)(SiO2)	Т		
	+ 0.16702E-02	Na6Si2O7	Т		
	+ 0.62628E-03	Na2O			
	+ 0.31176E-05	Na	Т		
********	+ 0.13324E-06	SiO2	-	****	****
DELTA H	I DELTA G DELT.	A V DELTA S	DELTA U I	DELTA A REA	ACT V
(J)	(J)	(I) (J/	K) (J) (J)	(1)
*******	******	******	******	******	***
-SISIG	1 <u>S1</u> G1				
207622 5	-804508 2 -0 245E - 10	232 201 2760/	1 5 -875180 7	$0.245E \pm 10$	
				= last line	

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0.90Na2CO3+0.10SiO2+O2+Ag+ (298.15K,1ATM,S1) (298.15K,1ATM,S1) (298.15K,1.0E-8ATM,G) (298.15	5K,1ATM,S1)
Ar = (208.15K.1ATM.G)	
(298.15K,1ATM,0)	
2.1635 mol (0.46222 O2	
+ 0.46222 Ar	
+ 0.75404E-01 CO2	
+ 0.13305E-C3 Ag	
+ 0.11799E-04 Na	
+ 0.21817E-05 NaO	
+ 0.18848E-05 O	
+ 0.36281E-06 CO	
+ 0.10786E-06 Ag2 T	
+ 0.72545E-09 O3	
+ 0.54816E-11 N22	
+ 0.24615E-20 SiO)	
(1473.00 K, 1.0000 atm, gas)	
+ 1.8312 mol (0.54594 Ag	
+ 0.40240 Na2CO3	
+ 0.31200E-01 (Na2O)2(SiO2) T	
+ 0.17181E-01 (Na2O)(SiO2) T	
+ 0.31134E-02 Na6Si2O7 T	
+ 0.15760E-03 Na2O	
+ 0.15768E-05 Na T	
+ 0.14411E-05 SiO2	
+ 0,35696E-06 (Na2O)(SiO2)2 T	
***************************************	******
DELTA H DELTA G DELTA V DELTA S DELTA U DELT	A A REACT V
(J) (J) (I) (J/K) (J) (J) (I)	
**********************	*****
-SISIGISIGI	
342485.5 -901544.4 -0.245E+10 298.469 320947.0 -923083.0 0.245	E+10
	line

0.90Na2CO3+0.10SiO2+O2+Ag+ (298.15K,1ATM,S1) (298.15K,1ATM,S1) (298.15K,1.0E-6ATM,G) (298.15K,1ATM,S1) Ar (298.15K,1ATM,G) 2.1635 mol (0.46222 02 + 0.46222 Ar + 0.75404E-01 **CO2** + 0.13305E-03 Ag + 0.11799E-04 Na + 0.21817E-05 NaO + 0.18848E-05 0 + 0.36281E-06 CO + 0.10786E-06 Ag2 Т + 0.72545E-09 O3 + 0.54816E-11 Na₂ + 0.24615E-20 SiO) (1473.00 K, 1.0000 atm, gas) 1.8312 mol (0.54594 Ag + + 0.40240 Na2CO3 + 0.31200E-01 (Na2O)2(SiO2) Τ + 0.17181E-01 (Na2O)(SiO2) Т + 0.31134E-02 Na6Si2O7 Т + 0.15760E-03 Na20 + 0.15768E-05 Т Na + 0.14411E-05 SiO2 (Na2O)(SiO2)2 Т + 0.35696E-06 + 0.21851E-28 Si) (1473.00 K, 1.0000 atm, liquid) + 0.00000 mol Ag Т (1473.00 K, 1.0000 atm, S1, a=0.45535) ******* ______ DELTA H DELTA G DELTA V DELTA S DELTA U DELTA A REACT V (J) (J) (I) (J/K) (J) (J)**(l)** -S1---S1---G1----S1----G1------342485.5 -912960.5 -0.245E+08 336.759 320947.0 -934499.1 0.245E+08 ================================ last line



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0.90Na2CO3+0.10SiO2+O2+Ag+			
(298.15K,1ATM,S1) (298.15K,1ATM,S1) (298.15K,1.0E-4ATM,G) (298.15K,1ATM,S1)			
Ar =			
(298.15K,1ATM,G)			
2.1635 mol (0.46222 O2			
+ 0.46222 Ar			
+ 0.75404E-01 CO2			
+ 0.13305E-03 Ag			
+ 0.11799E-04 Na			
+ 0.21817E-05 NaO			
+ 0.18848E-05 O			
+ 0.36281E-06 CO			
+ 0.10786E-06 Ag2 T			
+ 0.72545E-09 O3			
+ 0.54816E-11 Na2			
+ 0.24615E-20 SiO)			
(1473.00 K, 1.0000 atm, gas)			
+ 1.8312 mol (0.54594 Ag			
+ 0.40240 Na2CO3			
+ 0.31200E-01 (Na2O)2(SiO2) T			
+ 0.17181E-01 (Na2O)(SiO2) T			
+ 0.31134E-02 Na6Si2O7 T			
+ 0.15760E-03 Na2O			
+ 0.15768E-05 Na T			
+ 0.14411E-05 SiO2			
+ 0.35696E-06 (Na2O)(SiO2)2 T			
+ 0.21851E-28 Si)			
(1473.00 K, 1.0000 atm, liquid)			
+ 0.00000 mol Ag T			
(1473.00 K, 1.0000 atm, S1, a=0.45535)			
~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~			
DELTA H DELTA G DELTA V DELTA S DELTA U DELTA A REACT V			
(1)  (1)  (1/K)  (1)  (1)  (1)			
**************************************			
<u></u>			
$347485.5 = 074376.6 = 0.244E \pm 0.6 = 375.040 = 320047.0 = 0.45015.2 = 0.245E \pm 0.6$			

_____

0.90Na2CO3 + 0.10SiO2 + O2 + Ag +

(298.15K,1ATM,S1) (298.15K,1ATM,S1) (298.15K,0.21ATM,G) (298.15K,1ATM,S1) Ar =

(298.i5K,1ATM,G)

2.1635	mol ( 0.46222	O2			
	+ 0.46222	Ar			
	+ 0.75404E-01	CO2			
	+ 0.13305E-03	Ag			
	+ 0.11799E-04	Na			
	+ 0.21817E-05	NaO			
	+ 0.18848E-05	0			
	+ 0.36281E-06	CO			
	+ 0.10786E-06	Ag2	Т		
	+ 0.72545E-09	O3			
	+ 0.54816E-11	Na2			
	+ 0.24615E-20	SiO)			
	( 1473.00 K, 1	.0000 atm, gas)			
+ 1.8312	mol ( 0.54594	Ag			
	+ 0.40240	Na2CO3			
	+ 0.31200E-01	(Na2O)2(SiO2)	Т		
	+ 0.17181E-01	(Na2O)(SiO2)	Т		
	+ 0.31134E-02	Na6Si2O7	Т		
	+ 0.15760E-03	Na2O			
	+ 0.15768E-05	Na	Т		
	+ 0.14411E-05	SiO2			
	+ 0.35696E-06	(Na2O)(SiO2)2	Т		
	+ 0.21851E-28	Si)			
	(1473.00 K. 1	.0000 atm, liquid)			
	+ 0.00000 n	nol Ag	Т		
	(1473.00 K, 1	1.0000 atm, S1, a=	=0.45535 )		
		والمراجعة والمراجعة والمراجع والمراجعة والمراجعة والمراجعة والمراجعة والمراجعة والمراجعة والمراجعة والمراجع		حله حله حله حله حله حله حله عله عله حله عله عله ع	
DELIA	DELIAG DEL	LIAV DELIAS	DELIA U	DELIAA	KEAUT V
(J)	(J) (I) (J/K	.) (I) (I)	(U) ********************		*****
~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	····				

-S1---S1---G1----G1----

0.90Na2CO3+0.10SiO2+O2+Ag+ (298 15K 14TM S1) (298 15K 14TM S1) (298 15K 0 14TM G) (298 15K 14TM S1)
$\Delta r = $
(298.15K,1ATM,G)
2.1635 mol (0.46222 O2
+ 0.46222 Ar
+ 0.75404E-01 CO2
+ 0.13305E-03 Ag
+ 0.11799E-04 Na
+ 0.21817E-05 NaO
+ 0.18848E-05 O
+ 0.36281E-06 CO
+ 0.10786E-06 Ag2 T
+ 0.72545E-09 O3
+ 0.54816E-11 Na2
+ 0.24615E-20 SiO)
(1473.00 K, 1.0000 atm, gas)
+ 1.8312 mol (0.54594 Ag
+ 0.40240 Na2CO3
+ 0.31200E-01 (Na2O)2(SiO2) T
+ 0.17181E-01 (Na2O)(SiO2) T
+ 0.31134E-02 Na6Si2O7 T
+ 0.15760E-03 Na2O
+ 0.15768E-05 Na T
+ 0.14411E-05 SiO2
+ 0.35696E-06 (Na2O)(SiO2)2 T
+ 0.21851E-28 Si)
(1473.00 K, 1.0000 atm, liquid)
+ 0.00000 mol Ag T
(1473.00 K, 1.0000 atm, S1, a=0.45535)
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DELTA H DELTA G DELTA V DELTA S DELTA U DELTA A REACT V
(J) (J) (I) (J/K) (J) (J) (I)

-S1S1G1S1G1
======================================

•

0.90Na2CO (298.15K,1	3+ 0.10SiO2 + O2 + A § ATM,S1) (298.15K,14	g+ ATM,S1) (298.15K	,1.0ATM,G) (29	8.15K,1ATM	(,S1)
Ar (298.15K,1 <i>A</i>	= ATM,G)				
2.1635	mol (0.46222	O2			
	+ 0.46222	Ar			
	+ 0.75404E-01	CO2			
	+ 0.13305E-03	Ag			
	+ 0.11799E-04	Na			
	+ 0.21817E-05	NaO			
	+ 0.18848E-05	0			
	+ 0.36281E-06	CO			
	+ 0.10786E-06	Ag2	Т		
	+ 0.72545E-09	O3			
	+ 0.54816E-11	Na2			
	+ 0.24615E-20	SiO)			
	(1473.00 K, 1.	.0000 atm, gas)			
+ 1.8312	mol (0.54594	Ag			
	+ 0.40240	Na2CO3			
	+ 0.31200E-01	(Na2O)2(SiO2)	т		
	+ 0.17181E-01	(Na2O)(SiO2)	Т		
	+ 0.31134E-02	Na6Si2O7	Т		
	+ 0.15760E-03	Na2O			
	+ 0.15768E-05	Na	Т		
	+ 0.14411E-05	SiO2			
	+ 0.35696E-06	(Na2O)(SiO2)2	т		
	+ 0.21851E-28	Si)	-		
	(1473.00 K, 1	.0000 atm, liqui	d)		
	+ 0.00000 m	ol Ag	т		
	(1473.00 K, 1	.0000 atm, S1, a	a=0.45535)		
*******	********	*******	******	******	*****
DELTA I	H DELTA G DEL	TA V DELTA :	S DELTA U	DELTA A	REACT V
(J)	(J) (l) (J/K)) (J) (J)	(l)	*****	*******
-\$1\$1G	i1S1G1				
342485.5	-947208.8 0.213E+0)3 451,628 320	947.0 -968747.1	3 0.489E+0	2
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		=========	=======	==	