Activated Silica Sol as a Flocculant in Treatment of Mine Effluents

By

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A thesis submitted to the Faculty of Graduate Studies
and Research in partial fulfillment of the requirements
for the degree of Master of Engineering

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August 2002

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Abstract

Lime neutralization of acidic drainage is the most common process to produce an environmentally acceptable effluent. The process involves neutralization, precipitation of metal hydroxides, flocculation, settling and storage of the sludge. The sludge is not entirely stable over the long term due to the natural pH decline in the storage area that can re-solubilize metals. The use of activated silica sol could be an alternative to flocculants in the lime neutralization process. The nature of the metal hydroxide – silica bond could make the sludge more stable on short and long term.

It was observed that similar settling characteristics can be obtained with the standard flocculant and a low dosage of activated silica sol. Using activated silica sol, the settling rate is dependent on the concentration of magnesium and iron in the mine effluent.

There was an improvement in sludge stability when using a high dosage of activated silica sol. Two mechanisms have a role in the increased stability: the adsorption bond and the buffering capacity of activated silica sol. The tests suggested that a dosage of 0.1 $gSiO_2/gFe$ optimizes the settling characteristics and the sludge stability.

Résumé

La neutralisation à la chaux du drainage minier acide est la méthode la plus courante pour produire un effluent acceptable du point de vue environnemental. Le procédé comprend la neutralisation de l'acide, la précipitation d'hydroxydes métalliques, la floculation, la sédimentation et l'entreposage des boues. Les boues ne sont pas entièrement stables à long terme puisque le pH tend à diminuer naturellement dans l'aire d'entreposage et les métaux peuvent se re-dissoudre. Le sol de silice activée pourrait remplacer les floculants dans le procédé de neutralisation à la chaux. Le lien chimique entre les particules d'hydroxyde et de silice rendrait les boues plus stables chimiquement à court et long terme.

Des essais ont démontré qu'en utilisant un faible dosage de sol de silice activée les caractéristiques de sédimentation des boues sont semblables à celles obtenues avec un floculant traditionnel. Lorsque le sol de silice activée est utilisé, le taux de sédimentation est dépendant de la concentration de magnésium et de fer dans l'effluent acide.

La stabilité chimique des boues est améliorée lorsqu'un dosage plus élevé de sol de silice activée est utilisé comme floculant. Deux mécanismes sont impliqués dans cette augmentation de stabilité : soit le lien d'adsorption entre l'hydroxyde et la silice ainsi que l'effet tampon du sol de silice activée. Les essais ont permis de déterminer qu'un dosage de 0.1g SiO_2/g Fe correspond à une bonne sédimentation et une amélioration de la stabilité chimique des boues.

Acknowledgements

My first thanks are directed to my supervisor Professor Jim Finch for his guidance and support, as well as for his collaboration and understanding to allow me to perform the project outside the campus. Then I would like to acknowledge Professor Bruno Bussière, co-supervisor in Rouyn-Noranda, for good discussions and his help with the technicalities of the work.

The project was possible because of the much appreciated financial support by the Canadian Mining Industry Research Organization (CAMIRO) and the Chaire CRSNG – Polytechnique – UQAT en environnement et gestion des rejets miniers. I am also grateful to the four mines who gave me samples of their effluent to perform my work on.

Special thanks to Elias El-Ammouri for his advice on how to proceed with the project and his guidance throughout the past two years. Many thanks to the staff at URSTM (unité de recherche et services en technologie minérale): Nil Gaudet, Alain Perreault, Hugues Bordeleau, Mathieu Villeneuve, Benoît Plante and Mostafa Benzaazoua for the technical work and chemical analyses.

Finally, I would like to express my gratitude to my husband Paul for his support and editing help.

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Chapter 1: Introduction

1.1 Background

Acid mine drainage is a common phenomenon associated with the mining industry. It is a natural process occurring in locations where sulphur-bearing minerals are exposed to air and rain. Acid mine drainage is detrimental to aquatic life and results in loss of fish and flora [1, 2]. Mine workings, waste rocks, and tailings from sulphide mineral mines are prone to acid mine drainage. Table 1.1 presents the amount of acid-producing and potentially acid-producing tailings and waste rocks in Canada. Half of the acid-producing and potentially acid-producing tailings are located in Ontario, while more than half of the waste rock is in British Columbia, where large open pit mines were and are still in operation.

Pyrite is usually the most abundant mineral to oxidise to form acid mine drainage. Acid is produced from a sequence of reactions with the following overall reaction [3, 4]:

$$FeS_2 + 15/4\ O_2 + 7/2\ H_2O \rightarrow Fe(OH)_3 + 2SO_4^{-2} + 4H^+$$

The requirements for acid drainage generation are sulphur, water and oxygen. The presence of catalysing agents such as bacteria can increase the rate of acid generation. The acidic effluent produced accumulates metal ions by attacking metal-bearing minerals.

Various methods are used to reduce the impact on the environment. Acid mine drainage can be prevented or reduced by the application of dry and wet covers on the tailings pond and waste rock. In many cases, however, acid generation has already commenced and the effluent must be treated before release into the environment. Lime treatment is an effective, inexpensive option. A drawback is that treatment must be carried for over decades, maybe centuries till the acid producing minerals are exhausted. Other options, including reverse osmosis and ion exchange processes [5], are often too expensive and applicable to specific cases only.

The lime treatment raises the pH to precipitate the metal ions as hydroxides. A flocculant is added to promote settling and to produce a clear overflow. The sludge is pumped to a pond for long-term storage. However, the chemical stability of the sludges remains a concern. For example, the pH of rain water is sufficient to re-dissolve the metals.

Table 1.1: Estimates of Acid-producing and Potentially Acid-producing Mine Wastes In Canada [6]

	Tailings		Waste Rock
	million tonnes	hectares	Million tonnes
Newfoundland & Labrador	29.5	170	0.5
Nova Scotia	11.3	90	35.9
New Brunswick	76.5	564	25.7
Québec	254	2390	70.0
Ontario	984	6481	80.1
Manitoba	200	1780	68.8
Saskatchewan	66.4	273	19.9
British Columbia	192	571	421.0
Territories	64	243	17.0
Canada	1877.7	12562	738.9

1.2 Research project: activated silica sol

To improve sludge stability, the present study suggests the use of activated silica sol as the flocculant in conjunction with the lime. The hypothesis is that activated silica sol would adsorb the metal species and the metal – silica bond would create a more stable material. This would need to be achieved while providing similar settling characteristics as traditional flocculants.

Activated silica sol is used in municipal water treatment as a flocculant. Its application for the treatment of mine effluents has only been briefly tested prior to this thesis [7]. Activated silica sol is an inorganic polymer made of chains of silica molecules. It has the property to adsorb metal ions. The metal – silica bond thus created is believed to be more stable to pH variation than the metal hydroxide in the current sludges. Furthermore, it is non-toxic which makes activated silica sol an attractive option to stabilise the lime treatment sludge.

1.3 Objectives

The main objective of the project is to assess the performance of activated silica sol as a sludge stabilising agent. Specific objectives were set to meet the main objective:

1. Compare the settling characteristics of sludge produced by the lime neutralisation process when activated silica sol is used instead of a traditional flocculant.
2. Compare the chemical stability of sludge precipitated with activated silica sol to sludge precipitated with a traditional flocculant.

1.4 Thesis outline

The thesis is divided into seven chapters. Chapter 1 gives the background and the objectives of the project. Chapter 2 presents a literature review on the lime treatment of acid effluents and the properties of activated silica sol. Chapter 3 outlines the experimental procedures. In Chapter 4 the results of settling tests performed with a traditional flocculant and activated silica sol on simulated and fresh acid mine drainage are presented. Chapter 5 discusses the stability of the sludges. Standard leaching tests and humidity cell tests were performed on a standard flocculant-settled sludge and activated silica sol-settled sludge. Chapter 6 covers three complementary tests conducted to examine specific factors affecting the performance of activated silica sol. Chapter 7 summarises the conclusions and recommendations for further work.

Chapter 2: Literature Review

2.1 Introduction

This chapter reviews the processes used to treat contaminated mine effluents to produce an environmentally acceptable discharge. The common practice based on lime neutralisation, flocculation and settling is briefly discussed. The use of silica and activated silica sol is introduced along with details on the metal ion uptake (adsorption) mechanism. The basis of the project being sludge chemical stability, the final section of this chapter summarises an experiment that compares straight cobalt hydroxide sludge to a sludge formed by adsorption of cobalt on activated silica sol over a long period of time.

2.2 Lime neutralisation and precipitation process

The treatment of acidic water with lime is the conventional method used by the mining industry to produce an acceptable effluent. The main advantages over competing techniques are efficiency, reliability and low cost [8]. Each province has regulations concerning the quality of the effluent. In Québec, Directive-019 [9] dictates the maximum concentration of metals and chemical species in the final effluent of mine sites and the sampling frequency (Appendix 2).

The principle behind the use of lime is the formation of metal hydroxide precipitates. Lime in the form of hydrated lime ($Ca(OH)_2$) is preferred, either directly as a solid or as milk of lime. Other alkalis can be used, such as caustic soda and soda ash, but their cost and/or properties make them less attractive than lime [3, 8].

Hydrated lime also reacts with the acid (sulphate) component to form gypsum [3, 8]:

$$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 \cdot 2H_2O \qquad (2\text{-}1)$$

The more sulphate ions in solution the more gypsum is produced and can deposit in the tanks and pipes in the form of scale. Gypsum is formed more slowly than metal hydroxides [8].

Metal ions in solution exhibit a decrease in solubility with a rise in pH. Usually, acid mine drainage contains many different metal ions. The choice of pH for the treatment depends on the metal ions present. The selected pH should optimise the precipitation of all metal ions according to the solubility vs. pH properties (Figure 2.1). Hydroxide formation is generally

$$M^{+x} + xOH^{-} \rightarrow M(OH)_x \qquad (2\text{-}2)$$

Given the common presence of Fe^{3+} in acid mine drainage an important hydroxide precipitation reaction is

$$Fe^{3+} + 3OH^{-} \rightarrow Fe(OH)_3 \qquad (2\text{-}3)$$

Ferrous ions in solution form ferrous hydroxide, which is not very stable [10]. To avoid this, Fe^{2+} is oxidised to Fe^{3+} by addition of air (oxygen). Ferrous hydroxide reacts with air as follows [8, 10]:

$$Fe(OH)_2 + \tfrac{1}{2} H_2O + \tfrac{1}{4} O_2 \rightarrow Fe(OH)_3 \qquad (2\text{-}4)$$

Thus, typical lime treatment involves aeration, lime addition and thickening / clarification. The various engineered options based on these steps are described later.

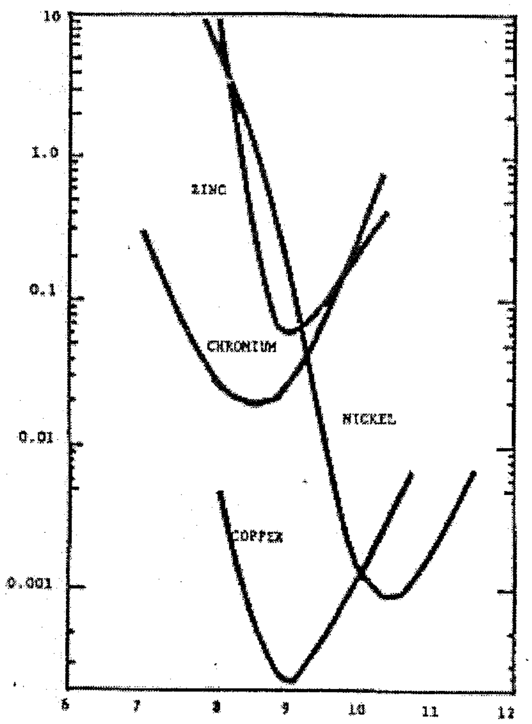

Figure 2.1: Solubility vs. pH diagram for several metal ions [2]

2.3 Flocculation and settling

To separate the metal hydroxide precipitate particles from the water, the particles must grow and settle. The flocculation process comprises three main steps [11]:

1. destabilisation of the fine particles by altering their surface charge to reduce the repulsion between particles;
2. floc formation and growth as the particles collide and aggregate;
3. floc breakage which regulates the maximum size of the flocs.

The use of polymers helps the flocculation process by reducing floc breakage, allowing the flocs to reach a larger size [11]. The flocculant attaches the hydroxide particles along its chain, creating a large aggregate particle (or floc) that resists breakage and settles quickly (Figure 2.2).

The dosage of flocculant is critical and plant specific. Too low an addition does not increase the settling rate while too much flocculant reduces the compressibility of the solid bed, and creates dispersion [10].

According to Hogg [11], settling rate is a function of floc size and the type of flocculant. Zinck and Aubé [10] observe that settling is affected by various factors, such as: pH, mixing, surface area and surface charge of particles, solid content of the slurry as well as the flocculant type used. Since these factors are either fixed (pH, mixing) or dependent on the water chemistry (surface charge and area), flocculant dosage is the parameter to manipulate to control the settling process [10].

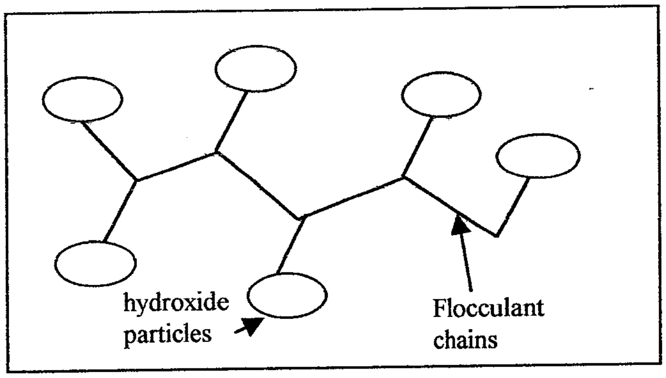

Figure 2.2 : Flocculation mechanism [12]

2.4 Processes for AMD treatment

The three most common lime treatment options are indicated in Table 2.1, and Figures 2.3 – 2.5.

Table 2.1: Summary of the treatment processes [5, 8]

Process	Advantages	Disadvantages
In-pond treatment: AMD is collected in a pond where lime is added (Figure 2.3)	• low cost • high retention time; no need for flocculants • good for low flowrates	• need large land space • ferrous oxidation difficult • high solids in suspension • 1 – 5 % solids in sludge • low lime efficiency; no mixing • no control over chemical reactions
Conventional treatment: mix tank for neutralisation and a clarifier for settling (Figure 2.4)	• ferrous oxidation • good control of effluent • low cost	• low density sludge: 1 – 5 % solids • large volume of sludge to store
High-density sludge process: a portion of the clarifier underflow is recycled and helps the neutralisation and settling (Figure 2.5)	• high density sludge: 10 – 30 % solids • lower volume to store • need less storage area	• high cost • requires closer control

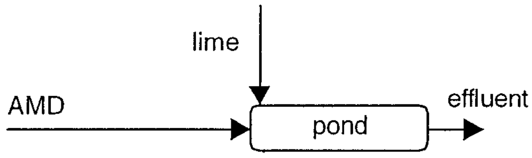

Figure 2.3 : In-pond treatment

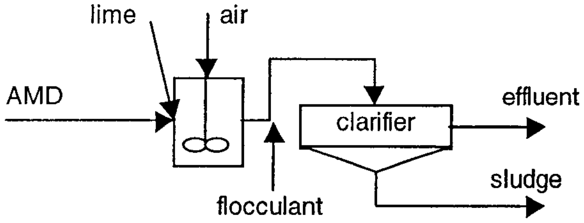

Figure 2.4 : Conventional treatment

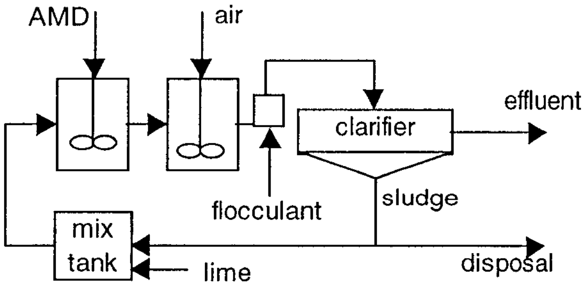

Figure 2.5 : High-density sludge treatment

An example of an HDS plant is at La Mine Doyon. The sludge density achieved varies between 15% and 22% solids and the neutralisation efficiency has increased since the replacement of the prior conventional process [13].

2.5 Sludge stability

The hydroxide sludge produced by lime neutralisation of acid water contains gypsum and unreacted lime. In the short term, the sludge remains alkaline and can buffer pH drift to acid and prevent the re-dissolution of metal hydroxides [3, 5].

In the long term, the neutralising components of the sludge become depleted. With no capacity to stabilize pH, the sludge pH decreases. Most metal hydroxides tend to re-dissolve when the pH moves below 7.5. Therefore, in contact with rain, metal ions may dissolve and contaminate the surface and groundwater [2].

In operating mines where the hydroxide sludge is stored with the mill tailings, stability is influenced by the acidity of the tailings [5] and by the presence of specific components, such as cyanide.

2.6 Silica

Silica has been used in various forms to remove metals from specific effluents for many years [14]. Metal ion removal with silica is by adsorption. The adsorption mechanism is a combination of ion exchange and electrostatic interaction.

The ion exchange explanation for the metal – silica bond was verified by several authors [15, 16, 17]. They observed a liberation of H^+ upon adsorption of a metallic ion on the surface of silica which indicates a cation exchange.

James and Healy [18, 19] and Palmer et al. [20] propose an electrostatic interaction mechanism. They observed that silica is negatively charged at alkaline pH and therefore electrostatically attracts the positive metal ion and monohydroxy (MOH^+) species. The adsorbed species are held to the silica surface by chemical or hydrogen bonding.

Whichever process (ion exchange or electrostatic interaction) or combination is responsible, adsorption onto silica occurs at lower pH than hydroxide precipitation. Schindler et al. [17] measured the range of pH over which there is adsorption (Table 2.2).

Table 2.2: Ion adsorption on silica vs. precipitation

Ion	pH range (adsorption)	pH range (precipitation)
Fe^{3+}	1 – 3	5 – 12
Pb^{2+}	4.5 – 7	7.5 – 10
Cu^{2+}	4.5 – 7	8 – 11
Cd^{2+}	6 – 9	11 and up

2.7 Sodium silicate

One form of silica is sodium silicate. Sodium silicate, $(SiO_2)_m \cdot Na_2O$, has different m values according to the ratio of the starting materials. In the case of effluent treatment, the desired sodium silicate is liquid and water soluble, corresponding to a "m" value of 3.22 [21, 22]. El-Ammouri [21] presented an extensive literature review on sodium silicate properties. The sections most relevant to the present work are discussed below.

When added to water, the surface of silica is hydrated, i.e., to form silanol groups, Si(OH). In water containing metal hydroxide ions, the silica and metal ions exchange a cation in the following reaction sequence [15, 21, 23]:

$$m(SiOH) \rightarrow m(SiO^-) + mH^+$$

$$M(OH)^{n+} + m(SiO^-) \rightarrow M(OH)(OSi^-)_m^{n-m}$$

overall: $$M(OH)^{n+} + m(SiOH) \rightarrow M(OH)(OSi^-)_m^{n-m}$$

where M is a metal ion and m and n are coefficients. Dugger et al. [15] proposed that the value of the coefficients m and n are the same and equal to the charge on the metal ion.

Tests done by Lempka [24] on the solubility of metal ions in water when treated with lime and sodium silicate gave the results presented in Table 2.3.

These results correspond to the pH ranges for ion adsorption measured by Schindler et al. (Table 2.2). Metals are adsorbed efficiently between pH 6 and 9.5 [24], which is almost the range of pH allowed for final effluent discharge to the environment (6.5 – 9.5), whereas lime alone removes metal species at pH 9 to 11.

Once precipitated, metal silicate sludge is resistant to pH variations; Figure 2.6 presents a general solubility vs. pH diagram for metal silicates [2]. In a sludge storage pond, silicate sludge is more stable over the long term than hydroxide sludge because it is less sensitive to pH variations. However, the adsorption process is reversible. With addition of acid to lower the pH well below neutral, the metal – silica complex dissociates.

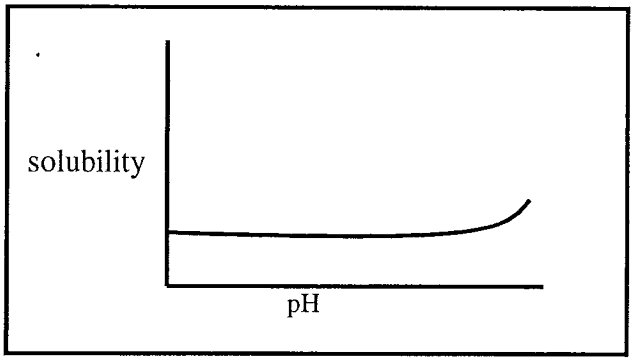

Figure 2.6: Solubility vs. pH diagram for metal silicates [2]

Table 2.3: Metal concentration in water (ppm) at different pH values after treatment with lime and sodium silicate [24]

pH	Ni	Zn	Pb	Cu
5.5	80.4	72.1	73.6	73.3
7	32.1	3.34	0.083	0.098
8	15.3	1.42	0.070	0.049
8.5	0.115	0.050	0.021	0.051
9	0.062	0.035	0.010	0.022
10	0.039	0.040	0.015	0.030

2.8 Activated silica sol

Activated silica sol has been used for many years in Canada's wastewater treatment plants as a coagulant aid [25]. Activated silica sol is prepared by mixing sodium silicate with water, followed by the addition of sulphuric acid to initiate a gelation process. The gelation is stopped before completion to produce a colloidal suspension, called stabilized or activated silica sol [21].

An activated sol is the structure prior to gel formation [26]. The end product is a negatively charged polymer (Figure 2.7) with a silica content between 0.5 and 1.0% [27, 28].

Silica sol is commonly produced by the Baylis Process, which uses sulphuric acid as the polymerization agent. Figure 2.8 is a simple flowsheet of continuous Baylis sol preparation [29].

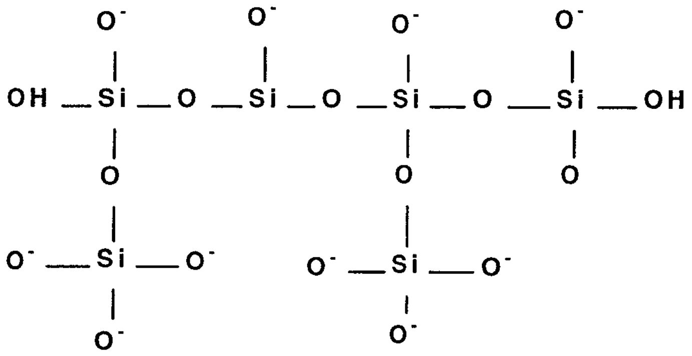

Figure 2.7: Activated silica sol polymer structure

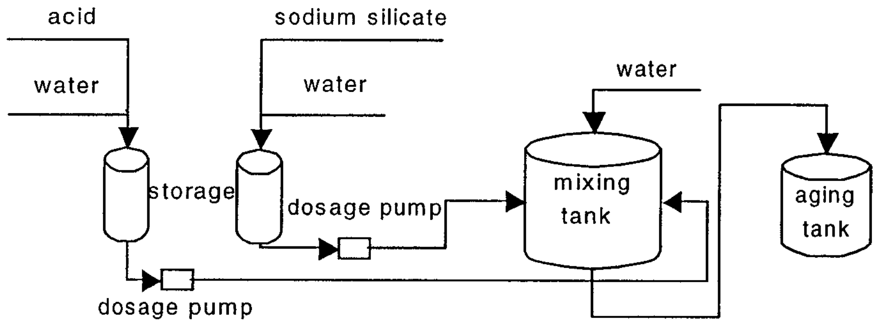

Figure 2.8: Baylis process flowsheet [29]

Gibson [25] observed that an addition of 3 to 4 ppm silica sol to a water treatment plant influent promoted rapid settling and low turbidity. Gibson explained the coagulation – flocculation mechanism with activated silica (Figure 2.9) as follows: the positively charged metal particles are destabilized by the long negative silica chain; the particles coagulate and are attracted to negative silica chain sites; the resulting particle's long tail hooks onto other flocs, further enhancing flocculation. This explanation follows the adsorption theory by electrostatic interaction, as described in section 2.7.

The flocs formed with activated silica sol should have a settling rate comparable to traditional flocculants to be of industrial interest. El-Ammouri [21] measured the settling rate on an iron-rich effluent. His results showed similar settling rates for silica sol and Percol (standard flocculant for AMD treatment). Other experiments by El-Ammouri et al. [23] on nickel-bearing solutions showed that high settling rates were achieved with silica sol.

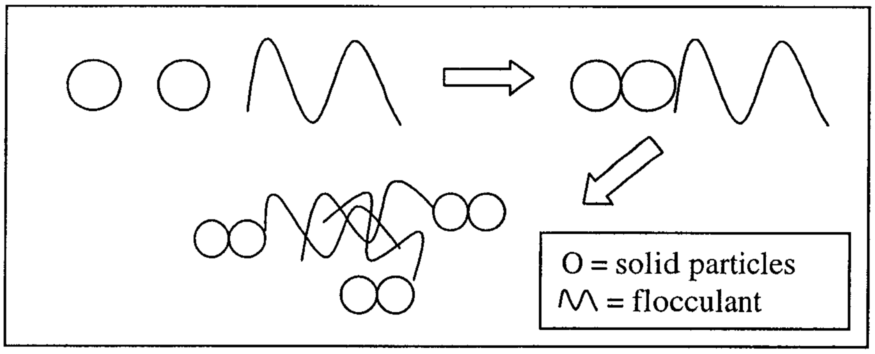

Figure 2.9: Mechanism of coagulation – flocculation [25]

2.9 Sludge stability with activated silica sol

Experimental evidence of the long term stability of the adsorbed metal complex was given by El-Ammouri et al. [30] using a cobaltous sulphate solution. Hydrated cobaltous ions are pink and the sludge formed when activated silica sol was used remained pink, indicating adsorption did not change the cobalt species. When lime is used to remove cobalt from solution, the sludge produced is green, being a mixture of blue cobaltous hydroxide and white lime and gypsum. After two years storage (in vials), the pink sludge with silica sol remained pink while the green lime precipitated sludge turned brownish, meaning a chemical change had occurred. The adsorbed cobaltous ions in the case of silica sol formed sludge were stable as observed by the lack of colour change over time.

The potential for increased sludge stability using activated silica sol as a settling aid is the focus of this thesis.

2.10 Summary

Acid mine drainage results from the oxidation of pyrite and other sulphides and the subsequent leaching of metals in the waste rock and tailings. It is arguably the most important environmental challenge facing the mining industry. Lime neutralisation of acid mine drainage was reviewed. The common process uses lime to raise the pH to precipitate metal hydroxides: $M^{+x} + xOH^- \rightarrow M(OH)_x$. At moderately alkaline pH, the hydroxides are mostly insoluble. They are separated in a clarifier or a pond with the aid of flocculants. The sludge produced is stored. Its short-term stability is attributed to the presence of unreacted lime and gypsum, but long-term stability is not confirmed.

Activated silica sols are used in wastewater treatment as a flocculant. Activated silica adsorbs metal ions forming a complex. Knowing that metal silicates are resistant to pH variation, the present work is designed to test the stability of the activated silica sol – metal hydroxide complex.

Chapter 3 : Experimental Procedure

3.1 Reagents

A series of acidic waters were prepared. The first tests were performed with laboratory-produced (simulated) acid water. Zinc sulphate ($ZnSO_4 \cdot 7H_2O$), copper (II) sulphate pentahydrate ($CuSO_4 \cdot 5H_2O$), iron (III) sulphate tetrahydrate ($Fe_2O_{12}S_3 \cdot 4H_2O$) and magnesium sulphate ($MgSO_4 \cdot 7H_2O$) were dissolved in deionized water at 18 megohm·cm. The balance of the tests were performed with mine effluents. Their complete analyses are included in Appendix 1. Table 3.1 indicates which water samples were used for which test, along with their collection date and principal metal concentrations.

The preparation of activated silica sol requires sodium silicate and sulphuric acid. The sodium silicate solution with SiO_2/Na_2O ratio 3.22 (called "N"), was from Fisher Scientific. The sulphuric acid (Fisher) preparation was diluted to 10 v/v%.

The lime was a suspension of hydrated lime ($Ca(OH)_2$) in deionized water (28 g lime / 1 L water).

Table 3.1: Source of acid water for the experiments (concentrations in ppm)

Test #	Source	Date *	Cu	Zn	Fe	Mg	Al	Comments
1,2,5,6	Simulated	12/12/2000	100	500	1000	-	-	-
3,4,7,8	Simulated	15/12/2000	100	500	1000	50	-	-
9-12	Simulated	3/01/2001	100	500	1000	100	-	-
R	Simulated	8/01/2001	100	500	1000	50	-	-
D1-D4	Doyon	12/02/2001	4	2	400	175	125	-
L1-L5	Laronde	20/02/2001	3	17	3.5	30	2	-
W1-W4	Waite Amulet	7/03/2001	0.7	4	240	100	14	-
13-16	Simulated	28/03/2001	100	500	1000	175	-	-
N1-N5	Mine N	2/04/2001	3.2	20	800	175	40	-
T1-T12	Mine N	7/05/2001	14	46	291	106	75	-
DM1-DM3	Doyon	13/09/2001	6.2	2.5	790	340	327	-
CHP-CHS	Doyon	13/09/2001	6.2	2.5	790	340	327	-
R1-R8	Doyon	30/10/2001	9.6	5.2	2786	944	1041	Dilution 4:1
C1-C8	Doyon	30/10/2001	9.6	5.2	2786	944	1041	Dilution 4:1

*: date prepared or collected

3.2 Flocculant preparation

The procedure used to prepare activated silica sol was provided by National Silicates Limited [29]. "N" sodium silicate was dissolved in deionized water (5 v/v %). While agitating, 10 v/v % dilute sulphuric acid was added to the sodium silicate solution. Agitation was stopped 45 s after acid addition and the solution was left for 9 minutes. The sol has a gel time of 18 minutes, and was stabilised at half its gel time. Stabilisation was achieved by dilution of the sol with 50 v/v % deionized water. The final product was 1.0% SiO_2 activated silica sol. The choice of the strength and fraction of gel time was based on previous work by El-Ammouri [21].

The standard organic flocculant chosen for comparison with activated silica sol was Percol. Percol E-10 was received in solid form from Laronde Mine and was dissolved in deionized water to yield a flocculant strength of 0.05% (0.05 g Percol / 100 mL water).

3.3 Settling tests

The acid waters were submitted to a standard lime treatment. One litre of water was placed in a 2-L beaker equipped with a ruler. Lime solution was added gradually while stirring to raise the pH to 9.7-10. The flocculant was then added and mixed for 30 s. Table 3.2 shows the flocculant conditions for each test. The agitator was stopped and the solid-liquid interface level was recorded at times up to 60 minutes. A solution sample was collected with a pipette from the clear portion of the solution (supernatant) after the hour to be analysed. The sludge was filtered on Whatman 4 filter paper and stored for later use.

Experiments R1 to R8 involved the recirculation of settled sludge to represent the high-density process. However, a typical plant recirculation ratio (sludge recycled per unit of fresh AMD) cannot be reproduced in the present laboratory set-up because of the excessive quantities of sludge required. Rather, acid water was submitted to the same lime treatment as described above. After an hour of settling, the water was decanted and the solids kept at the bottom of the container. Afterwards, a litre of fresh acid water was poured on the sludge and the lime treatment was repeated. This procedure was followed for four cycles. At the end, the sludge was weighed, dried for

2 to 3 days and weighed again to calculate the percent solids. Leaching tests were performed on the sludge.

Table 3.2: Flocculant addition for each test #.

1 ml ASS[1]	5 ml ASS	0.1 ml Percol	0.5 ml Percol	Calc from metal conc.	
				Percol	ASS
1,3,9,13	2,4,10,14	5,7,11,15	6,8,12,16,R	DM1-DM3	DM1-DM3
D1	D2	D3	D4	CHP	CHS
L1,L4	L5	L3	L2	R1,R2	R3,R4
W1	W2	W3	W4	R5,R6	R7,R8
N3	N4	N1	N2	C1-C4	C5-C8
T3,T7,T11	T4,T8,T12	T1,T5,T9	T2,T6,T10		

[1]: activated silica sol

3.4 Leaching tests

The leaching test protocol was based on the Modified Leachate Extraction Procedure [31], a standardized test used by Québec and Ontario. First, a portion of the sludge produced in the settling experiments was dried to determine the percent solids. In the present project, the mass of sludge produced was low, and the leaching test was performed with 2 grams of dry sludge. According to the percent solids of the sludge, deionized water was added to produce a 6.25% solids sludge. The sludge was agitated during the entire test. The pH was measured and adjusted with leachant addition to 5.0 +/- 0.2 after a 15 minute mixing time, then after 1, 3, 6 and 22 hours. The leachant was made of 60 wt% sulphuric acid and 40 wt% nitric acid. After 24 hours, the agitation was stopped, the volume adjusted to yield a 5% solids sludge with deionized water and the pH recorded. The sludge was filtered with a vacuum pump, the leachate prepared for analysis, and the solids dried and stored.

3.5 Humidity cell tests

A humidity cell (Figure 3.1) is an apparatus that accelerates the weathering of a solid sample compared to its natural weathering process. In the present study, the humidity cells were used to analyse the leachate obtained from a simulated sludge storage over time. The sludge was produced by the standard lime treatment. Because of the quantity of sludge required to fill the humidity cell, the final sludge samples used for the test were a combination of 20 L of the same acid water settled under the same conditions. One sludge sample was precipitated with 0.862 mL Percol while the other sludge sample was flocculated with 7.74 mL activated silica sol (dosage calculated from the metal content of the acid water). The sludge was dried before being placed in the humidity cell.

The test procedure is described in detail in ASTM D5744-96 [32]. A general outline is given.

First, a sample of the sludge was collected to determine percent solids, chemical composition, and specific gravity. The remaining sludge was placed on a filter paper in the humidity cell and was compacted. The test then began with a water flush; deionized water was dripped from the top of the cell, percolated through the sludge, left for half a day in contact with the sludge and was later collected from the bottom. The following analyses were performed on the leachate: pH measurement, metal content, redox potential, conductivity, acidity, alkalinity. Then, the weekly cycle began, the first 3 days with dry air (< 10% relative humidity) passed through the cell, followed by 3 days of wet air (~ 95% relative humidity) being circulated. The seventh day was a water flush (water passed through the sludge) and leachate analyses. This cycle was performed for 20 to 30 weeks. At the end of the test, the sludge was submitted to a similar characterisation as at the start of the test.

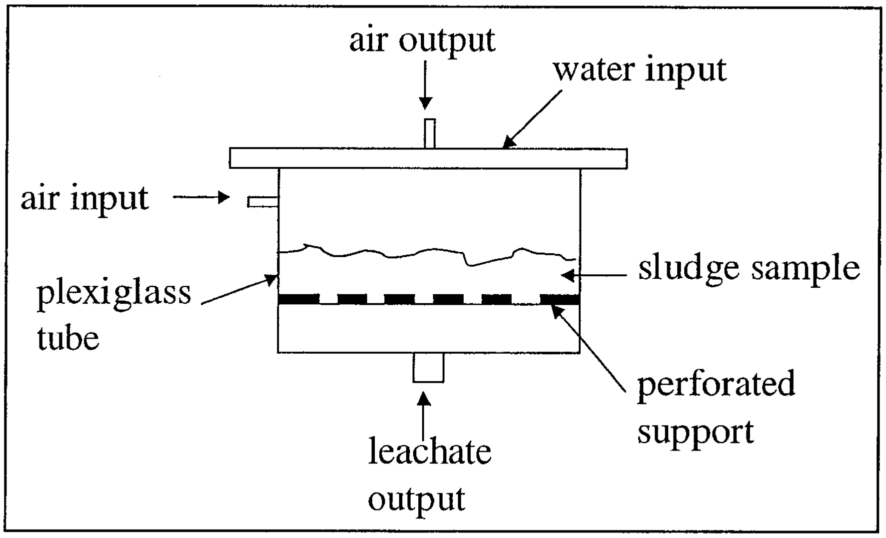

Figure 3.1: Diagram of a humidity cell

3.6 High temperature tests

In tests T1 to T12, the sludge was heated before going through the leaching test. The sludge samples were placed in beakers in a heat circulator for 24 hours. The beakers were covered to keep the sludge from drying. Three temperature settings were tested: 40°C, 50°C and 65°C. The sludge was then submitted to the leaching test as described.

3.7 Analytical techniques

The settling test supernatant (overflow) samples and the leachates (including from humidity cells) were analysed for metal content with an ICP-AA (induced coupled plasma – atomic absorption). The samples were first acidified by addition of nitric acid, following the standard 2% HNO_3 matrix for the analysis protocol. Dilutions were performed whenever the concentration of an element was outside the calibration range to improve the accuracy of the reading.

Two sludge samples were analysed for their metal content by a hydrofluoric digestion followed by ICP readings. The density of dry sludge was measured with a helium pycnometer (AccuPyc 1330).

All experiments and analyses were conducted in the URSTM laboratory (Unité de Recherche et Services en Technologie Minérale) in Rouyn-Noranda.

Chapter 4 : Settling Tests

4.1 Introduction

Settling tests were performed to compare the settling characteristics of lime treatment sludge flocculated with activated silica sol and with a standard organic flocculant. Acidic waters with various metal concentrations were tested to observe the behaviour of the systems.

Several variables were investigated to probe the mechanism by which activated silica sol acts as a flocculant at the dosages tested, such as the influence of magnesium and iron and the effect of the dosage on the settling characteristics (rate and compression). A microscopic examination of the settled sludge was performed.

4.2 Settling Tests

Lime treatment was conducted in a 2-L beaker, with the flocculant being either Percol E10 or activated silica sol. The solid-liquid interface level was tracked over an hour. The flocculant dosage was initially set as a volume, and was later converted to grams of flocculant per gram of metallic ions in the sample. The dosages are refered to as "conditions"; condition 1: 1 mL activated silica sol; condition 2: 5 mL activated silica sol; condition 3: 0.1 mL Percol and condition 4: 0.5 mL Percol. This allowed for a standardized experimental procedure and the testing of several flocculant dosages.

From the settling curves (Figure 4.1a), two parameters were estimated: the free-settling rate and the compression point. Most solid-liquid interface displacement occurs during free-settling. The compression point marks the beginning of the compression zone. The solids are now all settled and further thickening is achieved by water escaping through the voids between the flocs and inside the flocs themselves [33]. The measurement of the free-settling rate and the compression point can be done either directly from the settling curve (Figure 4.1a) or from a log-log plot of the settling curve (Figure 4.1b) when it is not obvious from the settling curve itself.

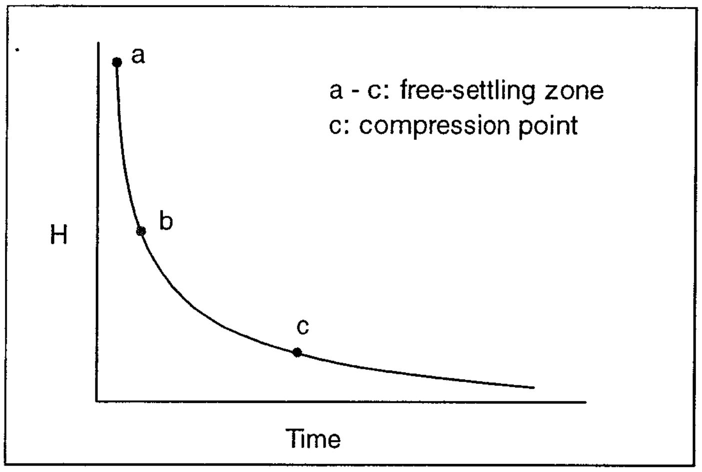

Figure 4.1a: Typical settling curve [33]

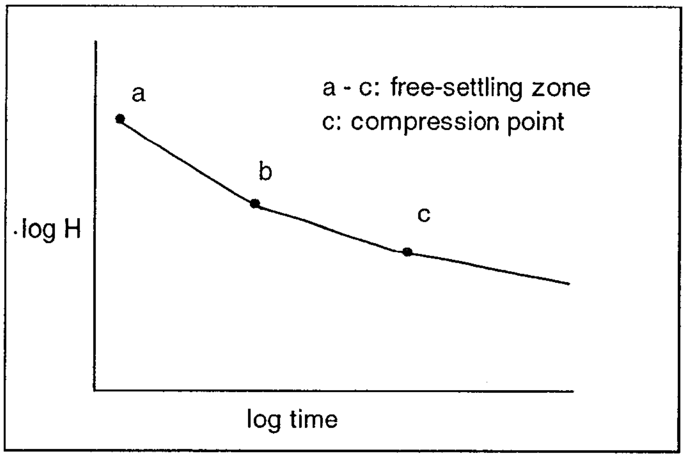

Figure 4.1b: Log-log plot of a typical settling curve [33]

4.2.1 Simulated effluent

The first series of tests were done with acid water produced in the laboratory. The metal content was 100 ppm Cu^{2+}, 500 ppm Zn^{2+} and 1000 ppm Fe^{3+}. These concentrations are on the high side (especially in copper and zinc) in comparison to most mine effluents.

The settling curves are presented in Figure 4.2. The initial part of the curves, where most of the interface displacement is achieved, has a similar slope for the four experiments. The final interface displacement, measured after 60 minutes, is a couple of mm higher when activated silica sol is used (lower on the graph because the displacement scale is inverted). From these observations, it can be concluded that activated silica sol works at least as well as Percol on simulated acid mine drainage.

The free-settling rate and compression point were estimated for the four conditions; the results are presented in Table 4.1 and Table 4.2. The highest free-settling rate was obtained with 5 mL activated silica sol, followed closely by 0.1 mL Percol. In terms of dosage by weight, the volume of flocculant used translates into low dosages due to the high concentration of metal ions in the water. Thus it can be inferred that 1 mL activated silica sol is not enough to flocculate efficiently. Too high dosage, such as 0.5 mL Percol, hinders the settling process.

The highest compression point was achieved with 1 mL of activated silica sol, i.e. in contrast to the settling rate the best condition is a low dosage.

The objective, to verify that activated silica sol behaves at least as well as Perol in terms of settling characteristics, was met for this simulated acid mine drainage.

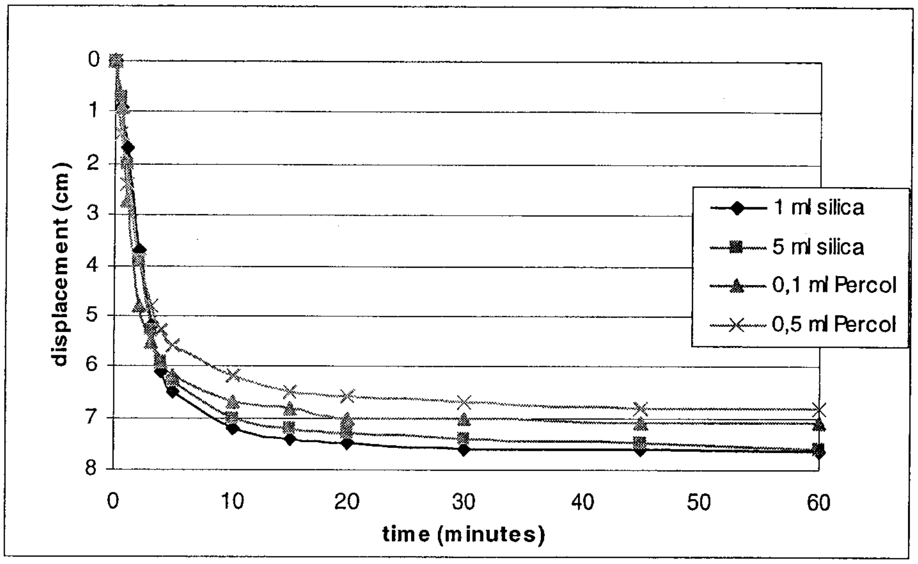

Figure 4.2: Settling curves obtained with simulated effluent, pH 9.7 with lime

Table 4.1: Free-settling rates for simulated effluent

condition	rate (cm/min)
1 mL ASS	0.49
5 mL ASS	0.70
0,1 mL Percol	0.67
0,5 mL Percol	0.43

Table 4.2: Compression points for simulated effluent

condition	comp.pt (cm)
1 mL ASS	7.4
5 mL ASS	7.0
0,1 mL Percol	6.7
0,5 mL Percol	6.5

4.2.2 Doyon effluent

Water from La Mine Doyon waste rock pile was treated with lime and submitted to the same four flocculant conditions. The water at pH 2.8 contained 4 ppm Cu^{2+}, 1.8 ppm Zn^{2+}, 400 ppm Fe^{3+} and 174 ppm Mg^{2+} (for a complete analysis refer to Appendix 1). The settling curves are presented in Figure 4.3.

The steepest slope was achieved with 0.5 mL Percol in the first five minutes of settling, whereas the other three conditions show similar initial rates. Overall, the settling is slower than for simulated acidic water. The presence of several metal species, especially magnesium, may contribute to this difference, as verified later (see section 4.3). The compression was higher with activated silica sol, as observed from the previous test with a simulated effluent.

The free-settling rates and compression points calculated from the settling curves are shown in Tables 4.3 and 4.4. The free-settling rates for three of the conditions are similar, but 0.5 mL Percol is definitely higher. However, the compression point is at the lowest (0.5 mL Percol). This test shows again a higher compression point with both dosages of activated silica sol over Percol. The high dosage of Percol (0.5 mL) can explain its fast settling rate and low compression point. With a high flocculant dosage, the flocculant can gather particles and create larger flocs that settle quickly. However, the water content in the flocs is greater and the sludge cannot compress as easily. Therefore, activated silica sol outperforms Percol in compression and is similar to a reasonable Percol dosage in terms of settlling rate for acid water from La Mine Doyon. The composition of the water varies with the season, the present test was performed with winter water.

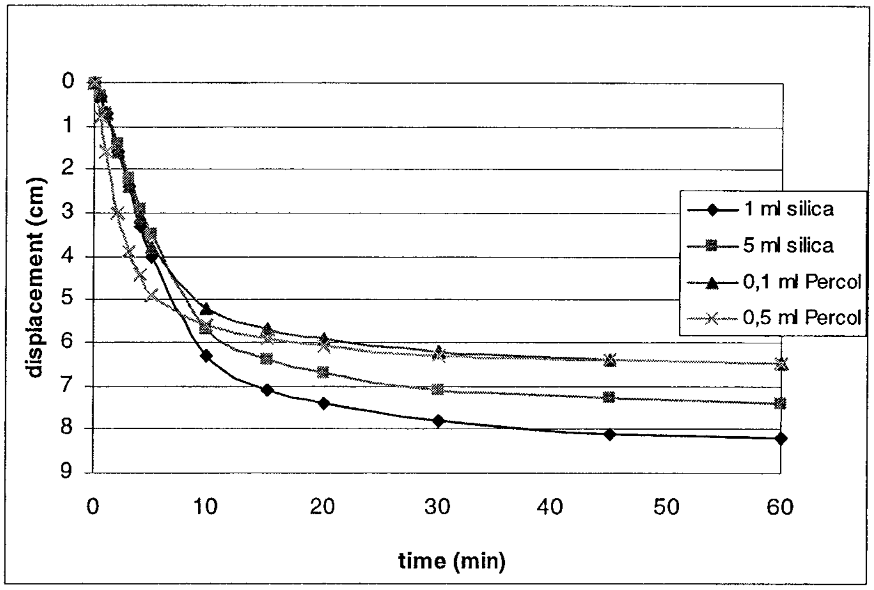

Figure 4.3: Settling curves obtained with Mine Doyon effluent, pH 9.7 with lime

Table 4.3: Free-settling rates for Mine Doyon effluent

condition	rate (cm/min)
1 mL ASS	0.55
5 mL ASS	0.50
0,1 mL Percol	0.52
0,5 mL Percol	0.83

Table 4.4: Compression points for Mine Doyon effluent

condition	comp.pt (cm)
1 mL ASS	6.6
5 mL ASS	6.0
0,1 mL Percol	5.2
0,5 mL Percol	5.0

4.2.3 Laronde effluent

Laronde Mine acid water has a relatively high pH (5) and a low metal concentration (3.5 ppm Fe, 3.1 ppm Cu, 16.6 ppm Zn). There were too few solids produced by the lime treatment to give a measurable interface. However, it was observed that the overflow water became clear in less time when Percol was used. It is believed that the iron concentration was too low to allow the activated silica sol to act as a flocculant.

The water sample was collected in a tank that gathers water from the underground mine and rain water from the surface of the property. This water sample provided a case where the use of activated silica sol instead of Percol is detrimental. A discussion of the influence of iron is included in section 4.3.

4.2.4 Waite Amulet effluent

Waite Amulet is a closed mine site with acid water being released from the tailings ponds. The water has a pH of 3, with 240 ppm iron, 100 ppm magnesium and 4 ppm zinc. The settling curves (Figure 4.4) are steeper than the previous tests. Both dosages of Percol have a higher initial slope than activated silica sol. The final interface displacement is similar for the four flocculant conditions.

The sludge produced was green, which is an indication that iron is present mostly as ferrous ions. (Water from Doyon and Laronde contained mostly ferric ions as their sludges were orange.) The treatment plant at the Waite Amulet site is shut down for the winter and the water is stored in a pond. Ice covered the pond at the time the water sample was collected, so the ferrous ions had no chance to oxidize to ferric. Within a few hours, the top layer of the sludge in contact with air changed from green to orange. Nevertheless, the settling tests were performed with ferrous ions.

The free-settling rates and compression points are given in Tables 4.5 and 4.6. The free-settling rates are higher with Percol, as well as the compression points. However, the compression points are all close, i.e. the difference in sludge density is minimal. The slower settling with activated silica sol can be attributed to the dominance of ferrous ions over ferric, as will be discussed in section 4.3.2. In an industrial plant, treatment usually includes an air addition point to convert ferrous to ferric ions during neutralisation. Therefore, ferric ions will dominate in most cases.

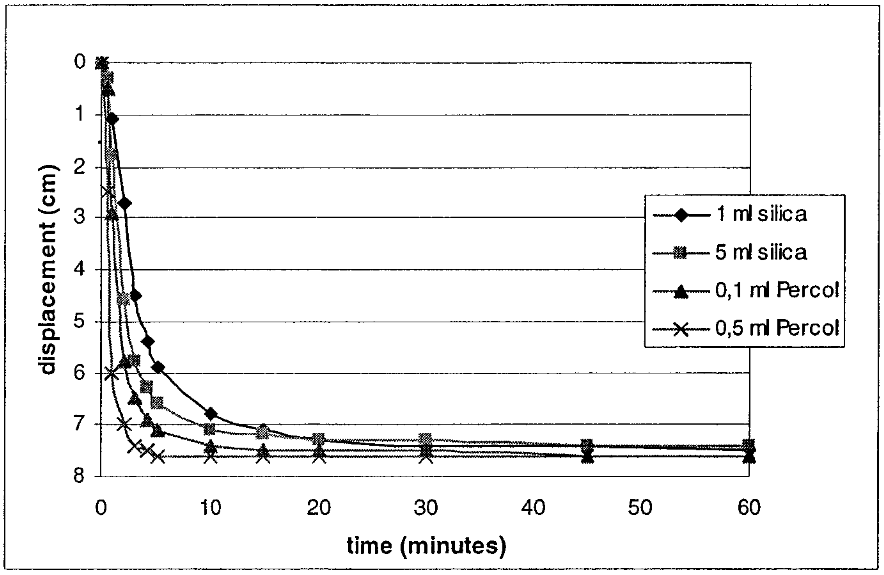

Figure 4.4 : Settling curves obtained with Waite Amulet effluent, pH 9.7 with lime

Table 4.5: Free-settling rates for Waite Amulet effluent

condition	rate (cm/min)
1 mL ASS	0.37
5 mL ASS	0.71
0,1 mL Percol	0.74
0,5 mL Percol	1.52

Table 4.6 : Compression points for Waite Amulet effluent

condition	comp.pt (cm)
1 mL ASS	7.3
5 mL ASS	7.1
0,1 mL Percol	7.4
0,5 mL Percol	7.5

4.2.5 Mine N effluent

The water collected at the closed mine N site had a pH of 2.8, 800 ppm iron, 175 ppm magnesium and 20 ppm zinc. Iron is present as ferrous, as determined by the green colour of the sludge. The settling curves (Figure 4.5) resemble the curves obtained with Waite Amulet water. The lines are very close to each other and exhibit a steep portion followed by a quasi-horizontal portion. The steepest slope in the first 5 minutes is given by 0.5 mL Percol. The final interface displacement is within 4 mm for the four conditions, a wider range than the test with Waite Amulet water.

Tables 4.7 and 4.8 present the free-settling rates and compression points for each curve. The 0.5 mL Percol dosage is probably too high since it has a very high free-settling rate and the lowest compression point by close to 1 cm. Activated silica sol had a comparable performance to 0.1 mL Percol, even a slightly higher free-settling rate and compression point in the case of 1 mL activated silica sol. Assuming that a dosage of 0.5 mL Percol is not desired with this water because of its detrimental effect on sludge compression, activated silica sol behaves at least as well as Percol with mine N spring water.

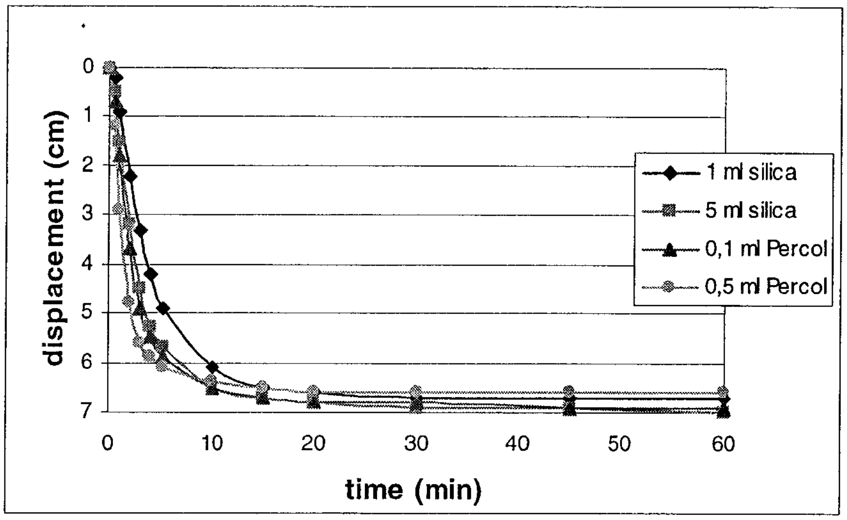

Figure 4.5: Settling curves obtained with mine N effluent, pH 9.7 with lime

Table 4.7: Free-settling rates for mine N effluent

condition	rate (cm/min)
1 mL ASS	0.45
5 mL ASS	0.33
0,1 mL Percol	0.43
0,5 mL Percol	1.14

Table 4.8: Compression points for mine N effluents

condition	comp.pt (cm)
1 mL ASS	6.7
5 mL ASS	6.6
0,1 mL Percol	6.5
0,5 mL Percol	5.7

4.3 Effect of specific metal ions

The testing of four different mine effluents provided some gauge to the influence of the metal species present. The four water samples had similar metal ion types but in different concentrations. The two that seemed to have an effect on the settling characteristics, especially when flocculated with activated silica sol, are magnesium and iron.

4.3.1 Magnesium

Settling tests were performed with simulated effluent with the same metal content as the original settling tests (100 ppm Cu^{2+}, 500 ppm Zn^{2+}, 1000 ppm Fe^{3+}) with an addition of 0, 50, 100 or 175 ppm Mg^{2+}. Magnesium may act as a coagulant that would improve the settling rate. The results presented in Figures 4.6 and 4.7 show otherwise; generally the water with no magnesium settled more rapidly. This effect is particularly apparent when 5 mL activated silica sol is used. The tests performed with Percol as the flocculant are more difficult to interpret but the case with no magnesium still has amongst the highest settling rates.

In order to obtain the best results with activated silica sol as a flocculant, it appears that water with minimal magnesium content is desirable. Table 4.9 correlates the mine effluents magnesium content to their best settling characteristics obtained with activated silica sol. They more or less follow the same trend as observed with simulated effluent.

From the experience in settling studies on quartz and sulphides [34] the coagulation role of magnesium is likely concentration and pH dependent. Coagulation tends to occur at $pH > 10$ where $Mg(OH)_{2(s)}$ forms and may induce coagulation by electrostatic bridging, but at high pH or concentration surfaces become coated with the positively charged $Mg(OH)_{2(s)}$ and mutual repulsion leads to dispersion. It is not clear if these findings apply to the hydroxide/gypsum systems here. Since most mine effluents are neutralised at pH around 9.5 and contain significant concentration of magnesium, coagulation is not promoted and settling may be retarded.

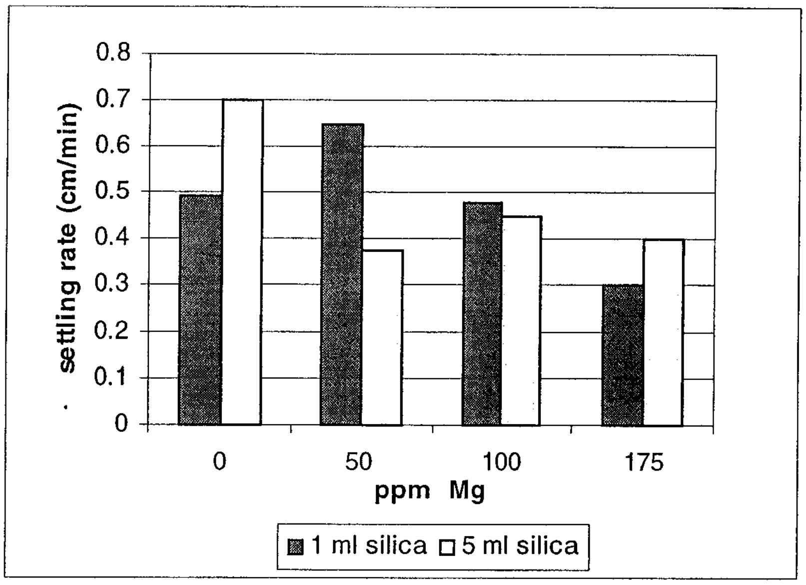

Figure 4.6: Settling rates of sludge precipitated with activated silica sol at pH 9.7 as a function of magnesium content of the acidic water

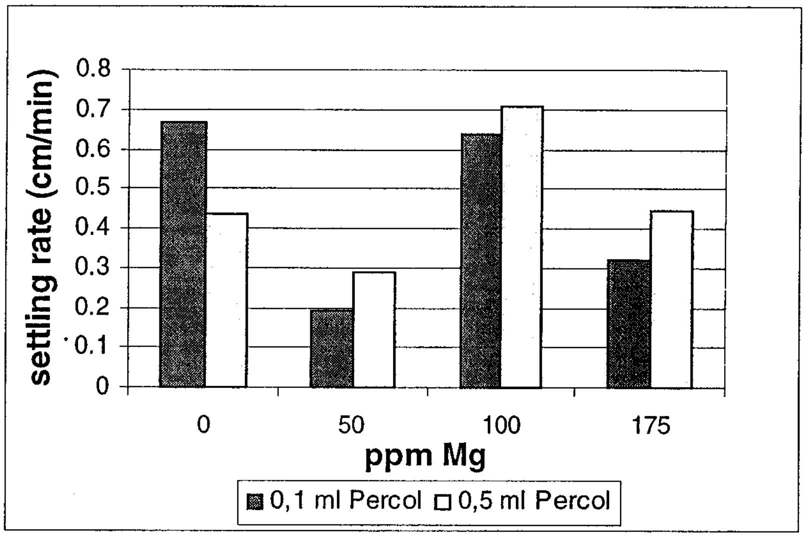

Figure 4.7: Settling rates of sludge precipitated with Percol at pH 9.7 as a function of magnesium content of the acidic water

Table 4.9: Settling rates and compression points of mine effluents related to the magnesium content

effluent	Mg^{2+} (ppm)	set.rate (cm/min)	comp.pt (cm)
simulated	0	0.70 (5 mL)	7.0 (5 mL)
Waite Amulet	100	0.71 (5 mL)	7.1 (5 mL)
Doyon	175	0.55 (1 mL)	6.6 (1 mL)
Mine N	175	0.45 (1 mL)	6.7 (1 mL)

4.3.2 Iron

Iron seems to be an important factor in the success or failure of activated silica sol as a flocculant. Laronde water, with only 3.6 ppm Fe^{2+}, showed poor settling when activated silica sol was used instead of Percol. The chemical reaction between iron and the silanol group is described as [35]:

$Fe^{3+} + Si(OH)_4 \rightarrow FeSiO(OH)_3^{2+} + H^+$ pH : 0.5 – 3.0

At pH > 3.0 : polymeric species are formed

The neutralisation of acid water is performed at high pH values, thus iron would form polymer chains with activated silica sol, which would help the settling process. Low concentrations of iron would not produce enough polymer chains to effectively settle the small solid particles. Therefore, a minimum of iron is required in the water to use activated silica sol efficiently as a flocculant. Waite Amulet water contained 238 ppm Fe^{2+} and showed good settling characteristics with activated silica sol. The other mine water samples had higher iron concentration, so a minimum value was not found.

Not only the presence of iron is important, but also the species in which it occurs in the water. This factor is more significant for laboratory-produced sludge.

Table 4.10 shows the settling rates obtained with the addition of 1 mL activated silica sol to the neutralized water as a function of the concentration of ferrous and ferric iron. The rates are lower when ferrous iron is present. Activated silica sol is known to interact more easily with higher valence ions [36], thus its effect is enhanced when ferric ions dominate over ferrous ions.

In terms of the potential application of activated silica sol, fortunately the industrial process of lime neutralisation involves an oxidation step to convert Fe^{2+} to Fe^{3+}. Air is injected in the neutralisation tank (or in a previous tank) to oxidize the ferrous ions. The purpose is to precipitate ferric hydroxide which is chemically more stable than ferrous hydroxide. To contemplate using activated silica sol in an industrial plant, the ferrous ions would have to be oxidized to ferric before the flocculant addition point.

Table 4.10: Comparison of settling rates with ferrous and ferric ions

Fe (II) ppm	**set.rate cm/min**
240	0.37
800	0.45
Fe (III) ppm	
400	0.55
1000	0.49

4.4 Flocculant dosage

The settling tests were performed with specific volumes of flocculant added to 1 L of acidic water. Another way to represent dosage is by mass of active flocculant per mass of metallic species present in the water. The conversion was made and related with settling rate and compression point.

4.4.1 Percol

The basis of the calculation for Percol is Percol strength is 0.05% (0.05 g /100 mL). The most important metal ions in acidic water were used in the calculation, i.e. Cu, Zn, Fe, Mg and Al. The dosages varied from 4.973 x 10^{-3} gP/gM to 3.125 x 10^{-5} gP/gM. These dosages are comparable to those used in industrial treatment plants for the same application [10]. Table 4.11 compares the settling rates to the dosage (numbered from highest to lowest). The two highest Percol dosages belong to Laronde water where no interface were measurable. The general trend is an increase in settling rate with increasing Percol dosage (i.e. in Table 4.11, decreasing rank number, 1 being highest dosage).

Table 4.11: Comparison between settling rate and Percol dosage

Test	set.rate (cm/min)	dosage (gP/gM)	rank
S5	0.43	$1.56\text{x}10^{-4}$	6
N1	0.43	$4.83\text{x}10^{-5}$	9
D1	0.52	$1.27\text{x}10^{-4}$	8
S1	0.67	$3.13\text{x}10^{-5}$	10
W1	0.74	$1.43\text{x}10^{-4}$	7
D5	0.83	$3.60\text{x}10^{-4}$	4
N5	1.14	$2.42\text{x}10^{-4}$	5
W5	1.52	$7.14\text{x}10^{-4}$	3

4.4.2 Activated silica sol

The same exercise was done for activated silica sol. Since iron proved to be an important parameter in the settling properties of activated silica sol, the dosages were calculated in terms of iron content of the water as well as total metal content (Cu + Zn + Fe + Mg + Al). The dosages thus obtained were ranked from highest (= 1) to lowest. The ranking was the same whether total metal or only iron was used in the calculation, therefore for simplicity the dosages are written as g SiO_2/g Fe. The silica content of activated silica sol was 1% for all tests.

Figures 4.8 and 4.9 show the settling rate and compression point as a function of the activated silica sol dosage. The settling rate data points are scattered and do not follow a trend. It was mentioned earlier that factors other than dosage can influence the settling rate, such as iron and magnesium content of the acidic water. The compression point follows a more consistent decreasing trend, suggesting that low dosages of activated silica sol are desirable for a more compact sludge. Two data points having a high dosage (> 2.9 g SiO_2/g Fe) were not included on the graph for scale clarity. They both gave a zero compression point.

In summary, activated silica sol can provide similar settling characteristics as Percol when used in low dosages, probably below 0.1 g SiO_2/g Fe. However, the magnesium and iron concentration in the water must be taken into account when choosing a dosage.

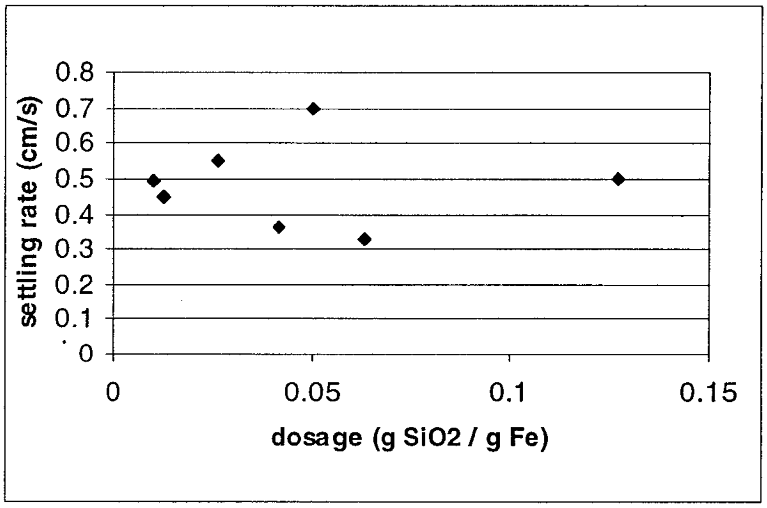

Figure 4.8: Settling rates as a function of activated silica sol dosage

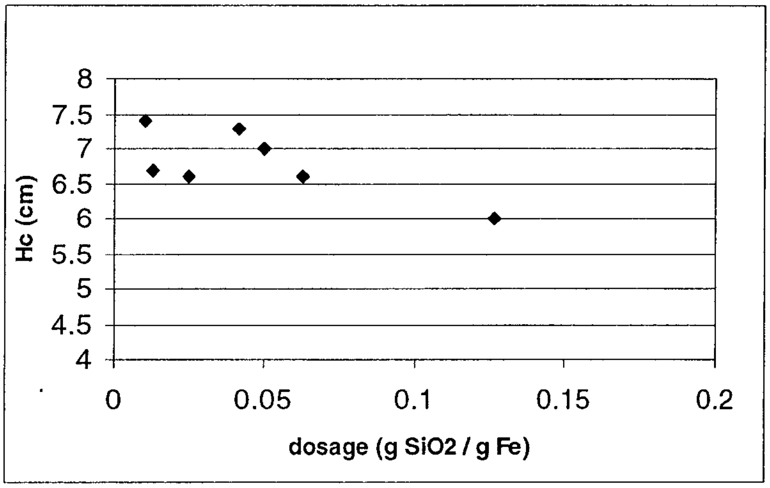

Figure 4.9: Compression points as a function of activated silica sol dosage

4.5 Microscopic examination

Dried samples of simulated effluent sludge (1 mL activated silica sol and 0.1 mL Percol) were observed under the scanning electron microscope (SEM). In both cases the metal distribution within the sludge is uniform. Copper is widely disseminated in both sludges as are iron, zinc and calcium. The silica in the activated silica sol-precipitated sludge is disseminated whereas it is segregated into a few areas in the Percol-precipitated sludge. Sulphur is associated with high calcium areas in both sludges. An analysis of these areas indicate the presence of crystalline gypsum with some Fe and Zn. At higher magnification, gypsum crystals are visible (Figure 4.10) either alone or in clusters.

In the literature it was mentioned that sludges are composed of an amorphous phase and gypsum and calcite grains [37, 38]. The amorphous phase contains the metal species. This fits the observations: the metals are uniformly dispersed in the amorphous matrix and sulphur and calcium are present in the gypsum crystals.

Samples of sludge produced from mine effluents were observed under SEM. The same observations were made: an amorphous phase that contains metal hydroxides, unreacted lime and gypsum with a crystalline phase made of gypsum rods (Figure 4.11). The use of activated silica sol as a flocculant in the lime treatment of acidic water does not change the morphology of the sludge.

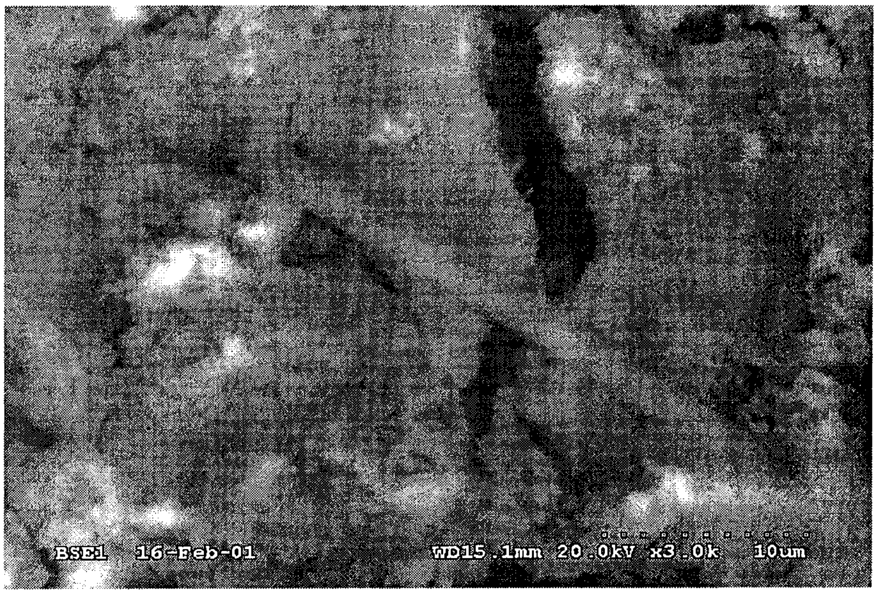

Figure 4.10: Gypsum crystal on an amorphous hydroxide matrix

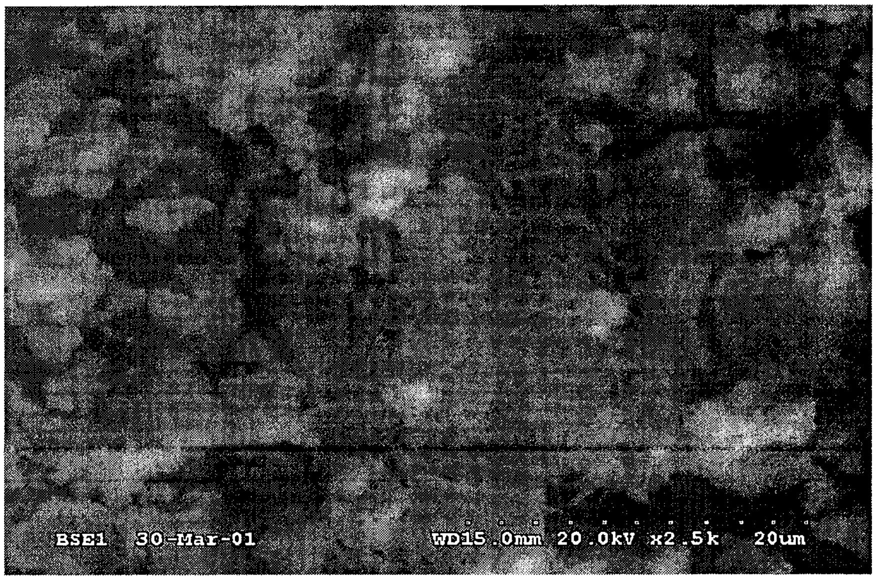

Figure 4.11: Cluster of gypsum rods on an amorphous matrix

Chapter 5: Leaching Tests

5.1 Introduction

This chapter describes the results obtained from the leaching tests. The objective of the tests was to compare the chemical stability, or leachability, of precipitated metals in the sludge. The sludge had been flocculated at different dosages with either Percol or activated silica sol.

The standard leaching test of 24 hours at pH 5 was performed on sludge produced from the settling tests. These tests permitted relationships to be established between flocculant dosage and sludge chemical stability. Leaching tests in humidity cells were also performed to test the long term stability of the sludge.

5.2 Leaching tests

The most important data gathered from the 24 hour leaching test were the metal concentration in the leachate and the final sludge pH. The metal concentration in the leachate is an indication of the leachability of the metal compounds and was used to compare the chemical stability of sludge precipitated with Percol versus activated silica sol. The final sludge pH is that at the end of the 24 hour test. The last pH adjustment to pH 5 was made 2 hours before the end of the test. The final pH value reflects the buffering capacity of the sludge.

The metal concentration in the leachates obtained from the tests were compared to the current Quebec regulation limits. The regulation has set concentration limits above which the sludge is considered a hazardous waste and must be disposed of accordingly. The limits for Quebec mine sludges are indicated in Table 5.1. These numbers vary between provinces and are subject to amendments [37].

Table 5.1: Maximum metal concentration in the leachate for the Modified LEP.

metal	conc. limit (ppm)
As	5
Cd	2
Cr	5
Cu	10
Ni	10
Pb	5
Zn	10

5.2.1 Simulated effluent sludge

The sludge produced with the simulated effluent contained significant amounts of copper and zinc. Thus, the copper and zinc concentrations in the leachate from the leaching tests were exceptionally high. No iron was leached. The copper concentration in the leachate for the four sludges precipitated with either activated silica sol or Percol is shown in Figure 5.1. There was roughly 10 times less copper leached when the sludge was precipitated with activated silica sol. The results for zinc are presented in Figure 5.2. The concentrations were very high (more than 100 times above the limit), making the results difficult to interpret. However, there was no clear advantage of using activated silica sol to increase the zinc stability of the sludge. The initial zinc content of the simulated effluent was probably too unrealistically high to yield meaningful leachability results.

Table 5.2 indicates the final pH values obtained for the four sludge samples. With activated silica sol as the flocculant, the pH of the sludge remained above 5.0 after 24 hours whereas the sludge precipitated with Percol fell below 4.8. This buffering effect of activated silica sol suggests greater chemical stability, which seems to be revealed in the case of copper.

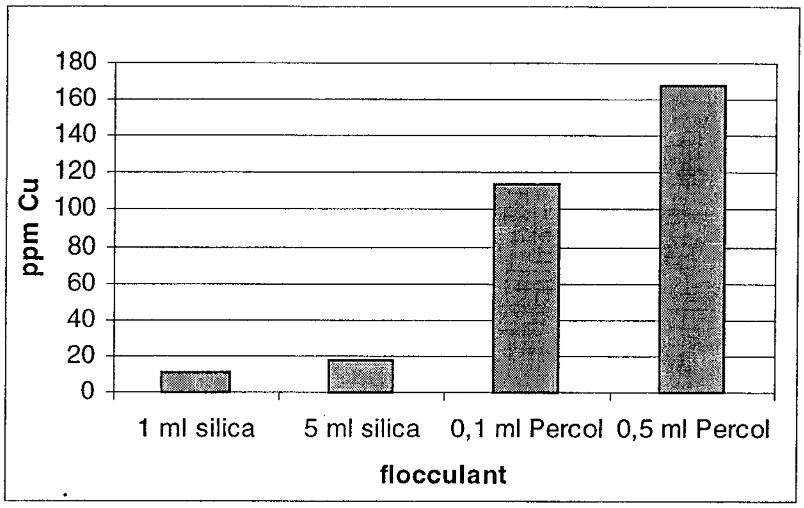

Figure 5.1: Copper concentration in the leachate for simulated effluent sludge

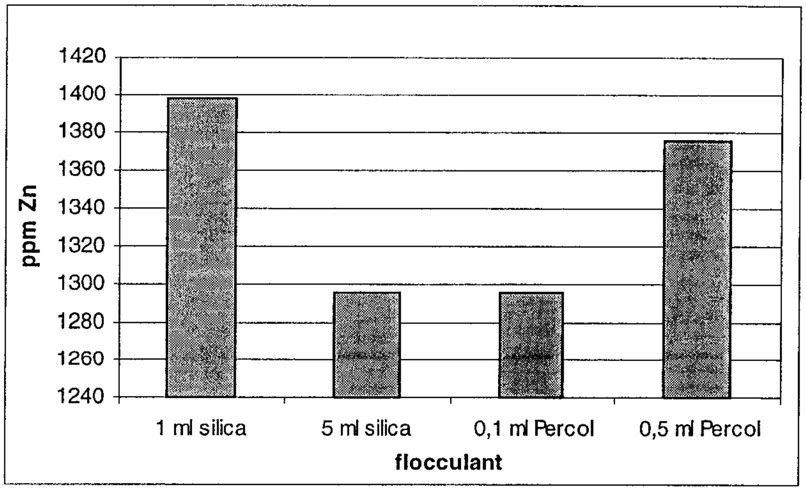

Figure 5.2: Zinc concentration in the leachate for simulated effluent sludge

Table 5.2: Final pH values for simulated effluent sludge leachate

Flocculant	final pH
1 ml ASS	5.24
5 ml ASS	5.08
0.1 ml Percol	4.64
0.5 ml Percol	4.39

5.2.2 Doyon effluent sludge

The sludge produced by the neutralization of Mine Doyon effluent provides a more realistic test. The sludge samples performed better in terms of the regulation, only the leachate from the sludge precipitated with 0.1 ml Percol was above the limit in zinc. The complete results for the four sludge types are presented in Table 5.3. The 0.5 ml Percol test was acceptable, its leachate was even below the concentration of the activated silica sol-precipitated sludge for copper, zinc and aluminum. The sludge precipitated with activated silica sol was more stable for Mg, Mn, Si, Na, Co, Ni, Cd. More calcium was leached, probably because more acid was added during the leaching test to bring the pH down to 5.0. Calcium dissolution could contribute to the improved buffering capacity of the sludge precipitated with activated silica sol by being the first component to dissolve under the action of acid.

The final pH of the sludge at the end of the 24 hour test also showed some enhanced buffering for the sludge precipitated with activated silica sol. Table 5.4 presents the final pH values for the four tests. The sludge flocculated with activated silica sol had a higher pH and more acid was required during the leaching test to set the pH to 5.0 (the same observations made with simulated sludge).

Table 5.3: Metal concentration in leachate, Doyon sludge

Metal	1 ml silica	5 ml silica	0,1 ml Percol	0,5 ml Percol
Cu	0.741	1.04	4.46	0.294
Zn	5.03	5.52	11	3.68
Fe	0	0	0	0
Al	7	11.2	44.3	4.53
Ni	2.01	1.55	3.27	1.82
Cd	0.039	0.034	0.064	0.038
Mg	1796	1796	2010	2133
Ca	2010	2418	817	887
Si	10.7	13	29.1	15.4
Mn	68.2	46.5	129.6	114.3
Na	47.7	40.4	80.4	57.7
Co	3.72	2.64	6.06	4.06
Ba	0.332	0.278	0.177	0.213

Table 5.4: Final pH values for Doyon sludge leachate

Flocculant	final pH
1 ml ASS	5.30
5 ml ASS	4.89
0.1 ml Percol	4.42
0.5 ml Percol	4.89

5.2.3 Laronde effluent sludge

Not enough solids were produced during a standard settling test with Mine Laronde effluent to track the interface and to yield the quantity of sludge required for the leaching tests. Therefore, the settling procedure was repeated on 7 litres of water for each sludge sample. Two types of sludges were produced; one with 5 ml activated silica sol as the flocculant and the second with 0.5 ml Percol as the flocculant. The leaching test was performed on each sludge type.

Laronde sludges failed the leaching test on copper, zinc and cadmium. The metal concentrations in the leachate are presented in Table 5.5. The activated silica sol did not improve the chemical stability of the precipitated metals; the performance of the sludge flocculated with activated silica sol was equal or worse than the sludge precipitated with Percol. The final pH was low for both sludge samples:. 4.49 for activated silica sol and 4.63 for Percol.

As was mentioned in sections 4.2.3 and 4.3.2, the low iron concentration in the acid water appears to have a detrimental effect on the flocculant ability of activated silica sol. It would appear that the uptake of metals onto activated silica sol did not take place, and thus, the sludge produced a metal-loaded leachate. Even the buffering effect observed with the simulated and Doyon effluents was not present with Laronde sludge. It is possible that the stabilizing effect of the activated silica sol is related to the degree of metal saturation of the adsorption sites.

Table 5.5: Metal concentration in leachate, Laronde sludge

Metal	5 ml silica	0.5 ml Percol
Cu	133	75.9
Zn	794	717
Fe	0	0
Al	11.6	11.2
Ni	4.22	4.31
Cd	2.57	2.31
Mg	520	644
Ca	2306	2551
Si	67.3	55.6
Mn	210	188
Na	105	96.3
Co	3.82	3.6
Ba	0.683	0.571

5.2.4 Waite Amulet effluent sludge

The pH of the sludge produced from Waite Amulet effluent had a tendency to drop dramatically. Table 5.7 shows the final pH obtained for the four flocculant additions. Throughout the test, the sludge precipitated with Percol showed a steady decline in pH. The .1 ml activated silica sol test was able to slightly recover from a low point of 3.72 up to 4.37 while the sludge precipitated with 5 ml activated silica sol maintained a pH above 6 for the entire leaching test and required more acid than the other three to set the pH to 5.0.

The 5 ml activated silica sol-precipitated sludge showed a definite improvement in chemical stability in Waite Amulet case. No copper, iron and lead were leached, along with very low amounts of zinc, nickel and cadmium. Table 5.6 presents the metal concentrations in the four leachates. The regulation limits were exceeded in zinc in the two sludges precipitated with Percol and the sludge flocculated with 1 ml activated silica sol.

The increase in chemical stability at the higher activated silica sol dosage suggests the number of adsorption bonds between silica and metal compounds is the key factor. This point is discussed further in section 5.3.2.

Table 5.6: Metal concentration in leachate, Waite Amulet sludge

Metal	1 ml silica	5 ml silica	0,1 ml Percol	0,5 ml Percol
Cu	0.824	0	1.673	0.676
Zn	52.2	0.939	40.5	37.5
Fe	0.163	0	0	0.369
Al	8.5	0.072	24.6	9.79
Ni	0.371	0.043	0.328	0.346
Cd	0.104	0.016	0.078	0.07
Pb	0.104	0	0	0.083
Mg	1010	787	917	991
Ca	1673	2684	2275	2163
Si	48.3	4.61	47.2	44.3
Mn	73.1	23.1	57	62.1
Na	21.4	24	14.8	21
Co	0.627	0.031	0.452	0.573
Ba	0.263	0.044	0.216	0.279

Table 5.7: Final pH values for Waite Amulet sludge leachate

Flocculant	final pH
1 ml ASS	4.25
5 ml ASS	6.79
0.1 ml Percol	3.79
0.5 ml Percol	4.27

5.2.5 Mine N effluent sludge

Only one of the sludge samples from Mine N effluent neutralization had a final pH above 4.8, and none above 5.0 (Table 5.9). Since all the pHs were low, the zinc concentrations were high, between 15 ppm and 48 ppm. The higher final pH belongs to the sludge precipitated with 5 ml activated silica sol, as observed with Waite Amulet sludge.

Table 5.8 presents the metal concentrations in the leachates. The sludge precipitated with 5 ml activated silica sol performed better in terms of chemical stability over the other sludge samples, but still failed the test in zinc. The lower dosage of activated silica sol (1 ml) produced the less stable sludge; its final pH was very low and it had the highest metal concentrations in its leachate. This observation coincides with the previous regarding the dosage of activated silica sol required to improve sludge chemical stability. The relationship between flocculant dosage in the neutralization step and the sludge chemical stability are discussed in the next section.

Table 5.8: Metal concentration in leachate, Mine N sludge

Metal	1 ml silica	5 ml silica	0,1 ml Percol	0,5 ml Percol
Cu	0.549	0	0.096	0.01
Zn	48	15	27.7	33.3
Fe	0	0	0.537	0
Al	14.3	0.462	1.13	1.75
Ni	0.211	0.155	0.19	0.207
Cd	0.144	0.078	0.106	0.116
Pb	0	0	0	0
Mg	969	1051	1051	1071
Ca	1480	1755	1459	1653
Si	49.3	24.8	23.4	29.1
Mn	79.8	83.7	88.8	90.3
Na	30.3	35.4	36.3	31.4
Co	0.665	0.419	0.524	0.577
Ba	0.459	0.418	0.415	0.447

Table 5.9: Final pH values for Mine N leachate

Flocculant	final pH
1 ml ASS	3.93
5 ml ASS	4.88
0.1 ml Percol	4.71
0.5 ml Percol	4.34

5.3 Flocculant dosage

The flocculant dosages referred to in this section are the same as those used to study the settling characteristics of the sludge. The dosages were transformed from volumetric to weight dosages, for Percol expressed as g Percol/g metal ions in the water and in g SiO_2/g Fe in the water for activated silica sol.

5.3.1 Percol

There was no noticeable relationship between Percol dosage and sludge stability. The final pH seemed to have a more important influence on the quality of the leachate than Percol dosage.

5.3.2 Activated silica sol

The results from the mine effluent sludges (except Laronde) were classified either as "unacceptable" or "acceptable" according to whether the copper and zinc concentrations in leachates exceeded the regulation limit or not, respectively. The flocculant dosage used in the settling stage is indicated beside the sludge. The data are presented in Table 5.10.

The tests classified as "acceptable" are those with the highest activated silica sol dosage per unit of Fe. Therefore, it would appear that a relationship exists between activated silica sol dosage and the sludge chemical stability. With a higher activated silica sol dosage, the number of adsorption bonds between silica and metal compounds is increased. The stability of this adsorption bond has been demonstrated by several authors, as discussed in Chapter 2.

Furthermore, the buffering effect demonstrated by the sludge precipitated with activated silica sol was more evident when the dosage was higher (Table 5.10). Activated silica sol influenced the sludge chemical stability not only by adsorbing metal but also by keeping the sludge pH at a higher value. The buffering is due to silica sol's known capacity to adsorb H^+ [39]. Since the solubility of metal hydroxides is dependent on pH, they are less likely to dissolve if the pH is kept high.

Overall, high activated silica sol dosage was beneficial to the sludge chemical stability. The action of activated silica sol was two-fold: it created adsorption bonds between silica and metal compounds, and its buffer effect kept the sludge pH high.

Table 5.10: Metal in leachate versus activated silica sol dosage, classified as "acceptable" and "unacceptable" leachate

"acceptable" leachate					"unacceptable" leachate				
Test #	dosage (gSiO_2/gFe)	ppm Cu	ppm Zn	final pH	Test #	dosage (gSiO_2/gFe)	ppm Cu	ppm Zn	final pH
D5	0.127	1.04	5.52	4.89	W1	0.0417	0.824	52.2	4.25
W5	0.208	0	0.939	6.79	N1	0.0125	0.549	48	3.93
N5	0.0625	0	15	4.88					
D1	0.0254	0.741	5.03	5.3					

5.3.3 Confirmation of dosage

From the results in Table 5.10, a flocculant dosage of 0.1 g SiO_2/g Fe was chosen as a possible optimum point for sludge stability. From a settling characteristics point of view such a dosage of activated silica sol is relatively high and not optimum (section 4.4.2). However, the right dosage for good settling characteristics was dependent on the water chemistry whereas the effect of specific metal ions such as magnesium were not an issue for the sludge chemical stability. Furthermore, the desired effect of using activated silica sol as a flocculant was more the improvement of the sludge chemical stability than good settling characteristics. Tests were performed to confirm that 0.1 g SiO_2/g Fe was indeed a good choice of activated silica sol dosage to provide good sludge chemical stability without too much deterioration in the settling process. As a comparison, a dosage of 3 x 10^{-4} g Percol/g

Metal was chosen for its good settling characteristics. Four tests were performed for each case to verify reproducibility.

5.3.3.1 Settling characteristics

The reproducibility of the settling and leaching tests was good, as demonstrated by the curves in Figure 5.3a and 5.3b, and the results for the four individual tests were averaged for each flocculant. The settling curves are shown in Figure 5.4 and the compression points and free-settling rates in Table 5.11. Percol performed better, especially on the short term. The final interface displacements were approximately the same for both flocculants, which is a better comparison point than initial settling rate for industrial purposes. Therefore, the chosen dosage of activated silica sol yielded similar final settling characteristics as Percol.

The low initial settling rate observed with activated silica sol could be due to magnesium. The water contained 236 ppm of magnesium, and such a high concentration was only noticed during results compilation. It was found from previous tests (section 4.3.1) that a high magnesium concentration slowed down the settling rate when activated silica sol was used as the flocculant.

Table 5.11: Compression points and free-settling rates for 0.1 g SiO_2/g Fe (ASS) and 3 x 10^{-4} g Percol/g M (Percol) with Doyon effluent

	Percol	ASS
Comp.pt (cm)	7.4	7.2
Fr-set rate (cm/min)	0.74	0.24

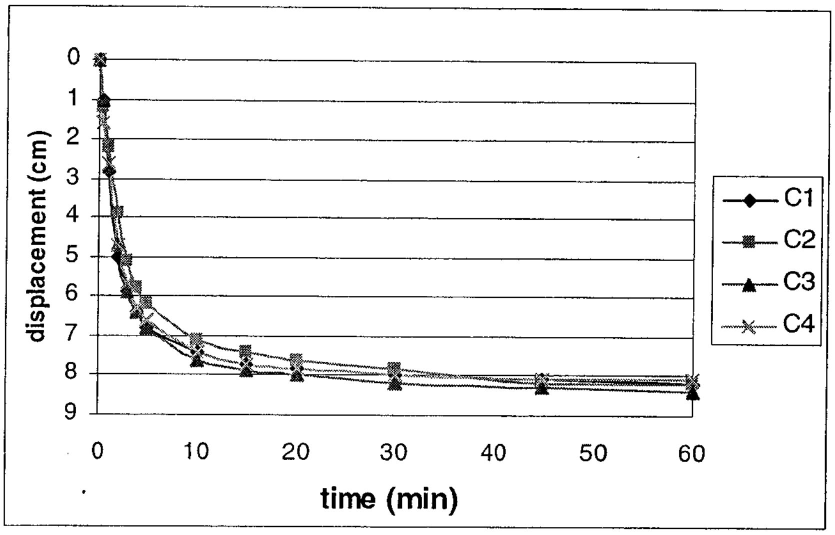

Figure 5.3a: Repeatability of settling test using Percol

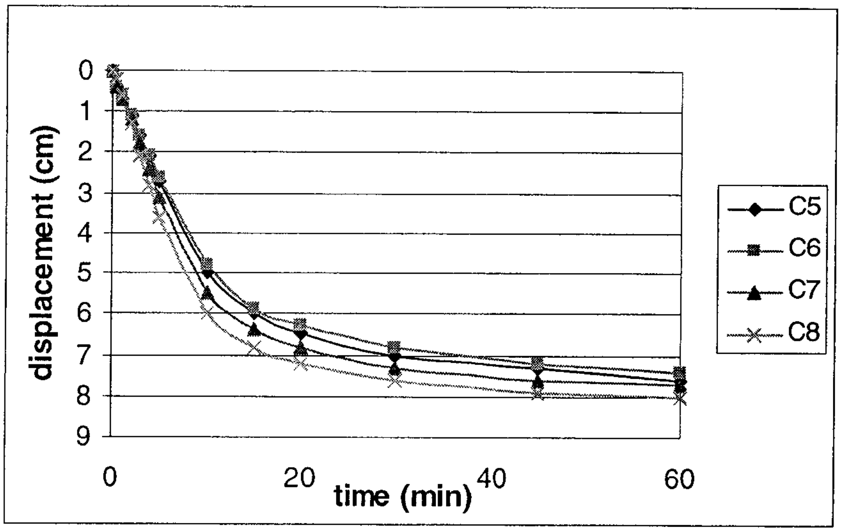

Figure 5.3b: Repeatability of settling test using activated silica sol

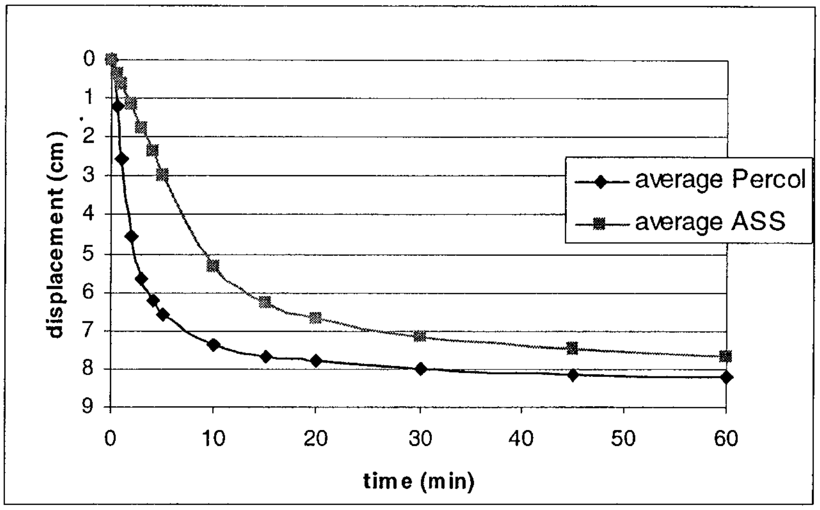

Figure 5.4: Settling curves for 0.1 g SiO_2/g Fe (ASS) and 3 x 10^{-4} g Percol/g M (Percol) with Doyon effluent

5.3.3.2 Sludge chemical stability

The leaching tests performed on the sludge precipitated with Percol (3 x 10^{-4} g Percol/g M) and activated silica sol (0.1 g SiO_2/g Fe) confirmed that the chemical stability is improved with activated silica sol. The average results of the four individual tests for each flocculant are presented in Table 5.12. Activated silica sol stabilized zinc significantly, and most metals in general. The average final pH was 4.61 for the sludge precipitated with Percol and 5.21 for the sludge precipitated with activated silica sol. The average final pH is a good indicator of the stabilization effect; the sludge flocculated with activated silica sol kept a significantly higher pH thus helping prevent metal species from dissolving.

Overall, the slight loss in settling rate with an activated silica sol dosage of 0.1 g SiO_2/g Fe was compensated for by a definite improvement in the sludge chemical stability when compared with sludge precipitated with 3 x 10^{-4} g Percol/g Metal, a typical Percol dosage.

Table 5.12: Metal concentration in leachate, Doyon sludge with 0.1 g SiO_2/g Fe (ASS) and 3 x 10^{-4} g Percol/g M (Percol)

Metal	ASS	Percol
Cu	0	0.533
Zn	0.822	2.343
Fe	0	0
Al	18.6	45.8
Ni	0.984	1.41
Cd	0	0.028
Pb	0	0
Mg	1915	1446
Ca	1753	2097
Si	20.9	24.4
Mn	33.6	31.9
Na	13.3	7.26
Cr	0	0
As	0	0.01

5.4 Humidity cell tests

Sludges precipitated with either Percol or activated silica sol were placed in humidity cells to observe their behaviour under a weak leachant (deionized water) over a long period of time (30 weeks). The following sections present the results from the weekly leach and the initial and final sludge characterization.

5.4.1 Leachate analyses

5.4.1.1 pH

Figure 5.5 shows the evolution of the leachate pH for the duration of the test. Both sludges had an initial peak and stabilized at around pH 8 after 30 days. The final pH was slightly higher for the sludge precipitated with activated silica sol, 8.19 compared with 8.08 for Percol sludge. This difference could be a result of the better buffering capacity of the sludge precipitated with activated silica sol. The pH results are well within the regulation limits, i.e. between 6.5 and 9.5 for a final effluent (see Appendix 2).

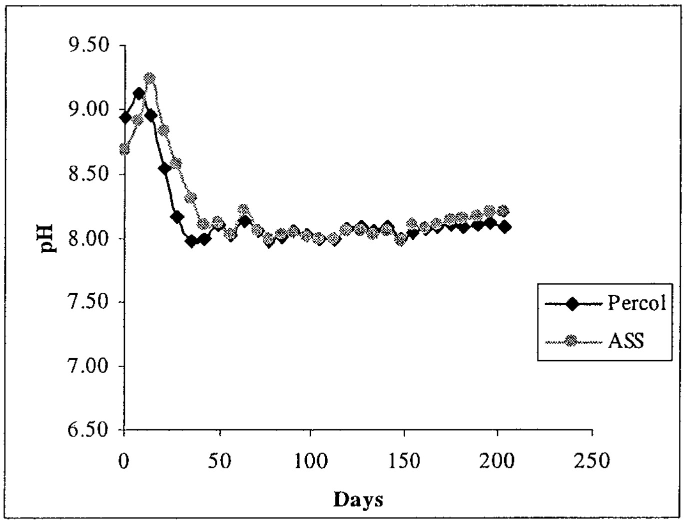

Figure 5.5: Leachate pH for the 30 week humidity cell test

5.4.1.2 Metal content

Four metal ions were significant in this experiment; zinc, iron, magnesium and calcium.

Zinc was not always present in the leachate and occurred in tenth or hundredth of ppm, which satisfies the regulation (max. 0.5 ppm Zn). Overall similar amounts of zinc were leached from both sludge types in 30 weeks; 0.85 mg for Percol and 0.87 mg for activated silica sol.

Iron occurred in the leachate for a week or two at the beginning of the test, then reappeared after 120 days in both sludge leachates.. The final leaching step yielded 0.01 ppm Fe from the Percol sludge and 0.03 ppm Fe from the activated silica sol sludge. The cumulative amount of iron leached is less in the case of the sludge precipitated with activated silica sol; 0.37 mg in 30 weeks versus 1.08 mg for the Percol sludge.

Magnesium is often associated with the neutralization capacity of the sludge. It is not included in Directive-019, so high concentrations in the effluent are less worrisome. Magnesium was present in the leachate starting day 30, it reached a maximum at 75 days for both sludges, and then the concentration decreased. The downward slope after 75 days was more important for the sludge precipitated with activated silica sol (Figure 5.6). Overall, around 1850 mg of magnesium were leached from both sludges (1858 mg for silica sol and 1843 for Percol).

Calcium dissolution is also an indication of a neutralization process taking place. More calcium was leached from the sludge precipitated with activated silica sol; 6057 mg compared with 5733 mg for the Percol-precipitated sludge. Figure 5.7 shows that leaching of calcium was more important early in the test and the calcium concentration in the leachate decreased with time.

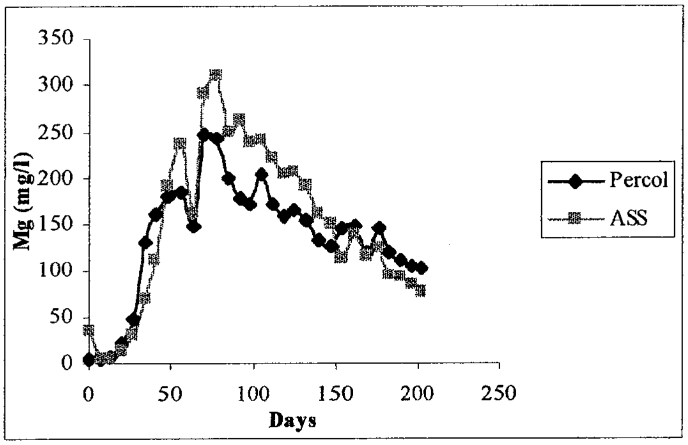

Figure 5.6: Magnesium concentration in the leachates

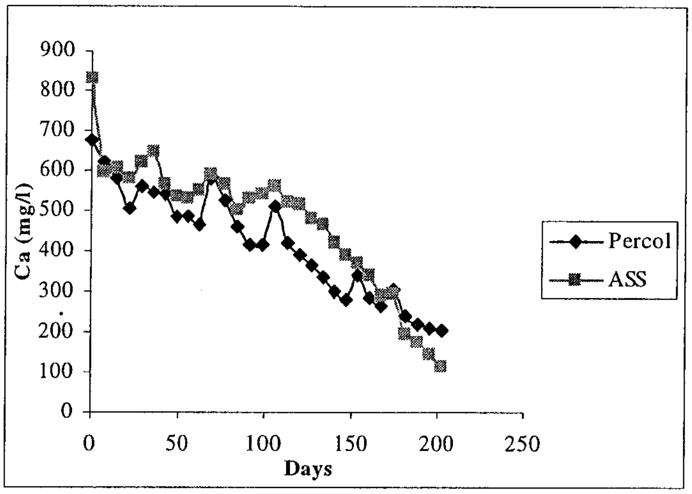

Figure 5.7: Calcium concentration in the leachates

5.4.1.3 Conductivity

Conductivity measurements indicate the presence of ionic species in the leachate. Figure 5.8 shows the results for the 30 weeks. Both leachates reached a maximum conductivity at around 80 days followed by a steady decrease that was more pronounced with the activated silica sol sludge. By comparison with Figure 5.6, it can be deducted that magnesium is probably an ion responsible for a major part of the leachate conductivity.

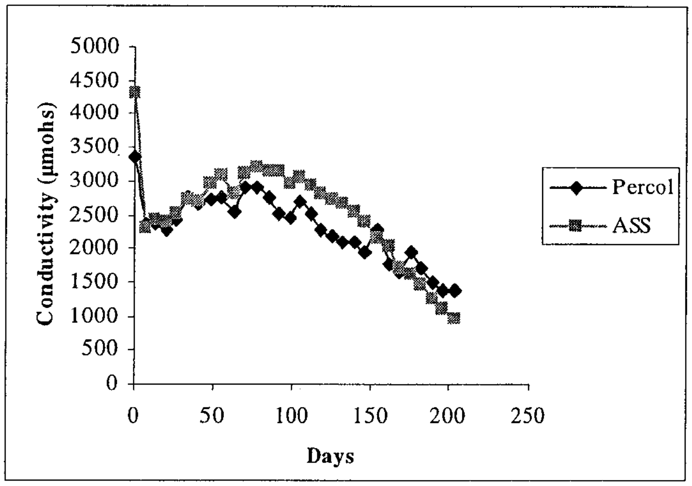

Figure 5.8: Leachates conductivity

5.4.2 Sludge analyses

The main components of the sludge at the beginning of the test were calcium, iron, sulphur, magnesium and aluminum. An analysis of the sludge after 30 weeks in the humidity cells gave essentially the same results except for sulphur and magnesium. Although calcium was heavily leached, it remained the main sludge component at 23 wt% for Percol and 26 wt% for activated silica sol. There was a decrease in the magnesium content, from 2.82% to 2.18% in the sludge precipitated with Percol, and from 2.52% to 1.79% in the sludge precipitated with activated silica sol. Magnesium was leached in abundant quantities from both types of sludge.

Sulphur accounted for around 4% of the initial sludges and dropped to levels below 1% after 30 weeks. Sulphur was released in the leachate as sulphate ion, which resulted in a pH decrease. However, neutralizing ions, such as Ca and Mg, balanced the sulphates to keep the pH relatively stable. Table 5.13 presents the initial and final sulphur concentrations. The drop at the end of the test was more important for the sludge precipitated with activated silica sol. Over a long period of time, this sludge would probably exhaust its acid-producing sulphates before the sludge precipitated with Percol and its effluent pH would remain higher.

Table 5.13: Sulphur content of the sludges (concentrations in wt%)

Sludge	Initial	Final
Percol	4.09	0.983
ASS	3.88	0.651

5.4.3 Conclusions

Both sludge types had regulation compliant effluents for the entire 30 weeks. Activated silica sol sludge gave a higher pH at the end of the test, more calcium was leached but less iron compared with the Percol-generated sludge. The sulphur content of the sludges dropped significantly during the 30 weeks, with a more important decrease in the sludge precipitated with activated silica sol. While both sludges are chemically stable under a weak leachant for 30 weeks, observations hints that the sludge precipitated with activated silica sol would remain stable for a longer period of time than Percol sludge.

Chapter 6: Complementary Tests

6.1 Introduction

Chapter 5 demonstrated the advantage of using activated silica sol to increase the sludge chemical stability. Chapter 6 presents three experiments to complement the settling and leaching tests performed. The first experiment discussed is one in which the sludge was heated before being submitted to the regular leaching test. The second experiment involved the combination of Percol and activated silica sol as a single flocculant addition followed by the standard settling and leaching protocol. The last experiment involved recycling of the sludge over 4 cycles to simulate the high density sludge process. The "recycled" sludge was then tested for chemical stability.

6.2 Elevated temperature

6.2.1 Introduction

It was postulated that activated silica sol could begin to turn into a "glassy" structure when heated, which would further retard metals from dissolving when in contact with an acidic leachant. Although the temperatures are well below those of glass formation, any structural change in that direction could be beneficial. Water from mine N collected on May 7, 2001 was used for these tests. It contained 46 ppm Zn, 14 ppm Cu (the highest of the effluents tested in this project), 291 ppm Fe and 106 ppm Mg. The usual lime treatment protocol was followed, with the same flocculant conditions as previously described: 1 ml ASS, 5 ml ASS, 0.1 ml Percol, 0.5 ml Percol. Each flocculant condition was tested three times, for a total of 12 tests. The sludge produced was heated for 24 hours at 40°C, 50°C and 65°C. Leaching tests were performed on the heated sludge.

6.2.2 Metal concentration in the leachate

The metals that occurred in significant concentration in the leachate were copper, zinc, magnesium, calcium, manganese, sodium and silicon. The elements considered specifically to compare leachability are copper and zinc. The results are presented in Table 6.1 (flocculation with activated silica sol) and 6.2 (flocculation with Percol). The blank spaces indicate a non-valid test (acid overdosage).

The metal concentrations are high for all tests. Table 6.1 shows that no improvement in chemical stability was observed with a rise in temperature for the sludge precipitated with activated silica sol. However, for Percol (Table 6.2) the reverse is true; the copper and zinc content of the leachate decreased with temperature.

The desired effect of increased chemical stabilization with heating was not found with sludge flocculated with activated silica sol. It was hoped that some beneficial changes in structure would occur, but the experiment showed that, if anything, changes that occur are detrimental.

In the case of Percol, a temperature rise seemed to improve the sludge chemical stability. The reason is unknown and was not investigated.

Table 6.1: Copper and zinc concentrations in the leachate of sludge precipitated with activated silica sol submitted to a leaching test

Silica sol	Temperature	ppm Cu	ppm Zn
1 ml	40	0.63	66.7
1 ml	50		
1 ml	65	0.664	137
5 ml	40	4.57	218
5 ml	50	0.705	156
5 ml	65	1.22	233

Table 6.2: Copper and zinc concentrations in the leachate of sludge precipitated with Percol submitted to a leaching test

Percol	Temperature	ppm Cu	ppm Zn
0,1 ml	40	1.73	127
0,1 ml	50		
0,1 ml	65	0.739	99.9
0,5 ml	40	1.95	138
0,5 ml	50	0.486	88.7
0,5 ml	65		

6.2.3 Conclusions

There was no improvement in sludge chemical stability with heating when activated silica sol was used as the flocculant. The effect of elevated temperature was even detrimental to sludge stability.

6.3 Combination of Percol and activated silica sol

6.3.1 Introduction

A combination of Percol and activated silica sol it was postulated might combine the advantageous settling characteristics of the Percol and chemical stability of the silica sol.

Acid water from La Mine Doyon waste rock pile was used for the tests. The water contained 800 ppm iron, and this value was used to set the flocculant dosage. From previous tests, optimum dosage for good settling and good chemical stability were, respectively, 3×10^{-4} g Percol/g metal ions and 0.1 g SiO_2/g Fe. The tests described in this section used the following combinations:

Test 1: 50P/50ASS: 1.5×10^{-4} g Percol/g M
0.05 g SiO_2/g Fe
i.e. 50% of each optimum flocculant dosage
Test 2: 25P/75ASS: 0.75×10^{-4} g Percol/g M
0.075 g SiO_2/g Fe
Test 3: 75P/25ASS: 2.25×10^{-4} g Percol/g M
0.025 g SiO_2/g Fe

6.3.2 Settling characteristics

The settling curves are presented in Figure 6.1. With more Percol, the settling was slower, which is opposite to the observation for Percol alone. However, the flocs were visibly smaller in the presence of activated silica sol, and small flocs settle less rapidly. There appears to be an interaction between Percol and activated silica sol when used together that prevented the Percol from being as effective as when used alone.

When compared with the one flocculant at a time tests, the combination of Percol and activated silica sol yielded a lower compression point, thus a lower sludge density. As seen in Figure 6.2, the settling was slower for the best of the combination tests than for activated silica sol alone. The acid water used for the combination tests contained 340 ppm of magnesium, which has an impact on settling. In section 4.3.1, it was noted that magnesium slowed down settling but did not influence the compression point. The high magnesium concentration of the water probably explains the slow settling but does not account for the lower compression point. Again, there appears to be an interaction between Percol and activated silica sol.

In conclusion, the combination of Percol and activated silica sol did not improve the settling characteristics of the sludge.

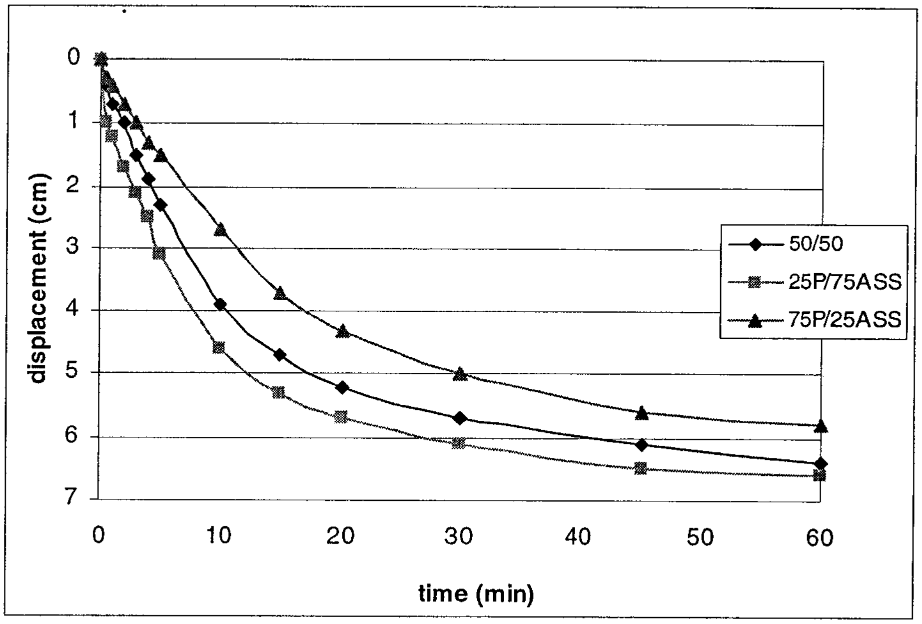

Figure 6.1: Settling curves for the three combination tests, pH 9.7 with lime.

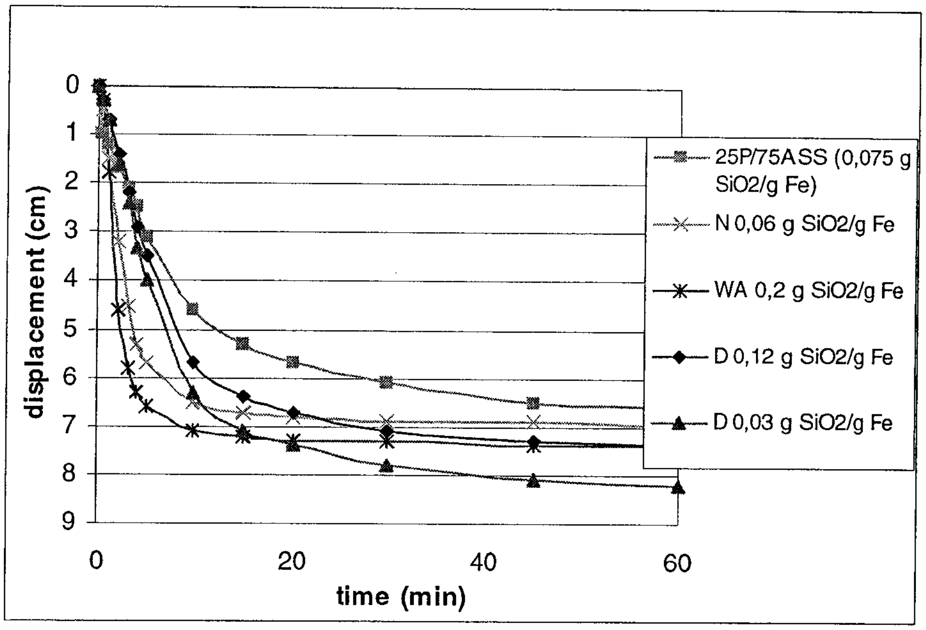

Figure 6.2: Comparison of settling curves, tests with different water samples at different activated silica sol dosages, pH 9.7 with lime.

6.3.3 Chemical stability

In terms of chemical stability of the sludge, the results were more encouraging. For the three tests, the pH stayed above 5.00 for the entire 24 hours, and the leachates (Figure 6.3) were well within the regulation limits.

The leachate of the 25P/75ASS test was compared to leachate from previous tests with activated silica sol alone as the flocculant. Table 6.3 shows the results. The leachate from 25P/75ASS had among the lowest metal concentration, especially for zinc, which was generally the most leachable metal. The two Doyon leachates were high in zinc, but still below the limit of 10 ppm.

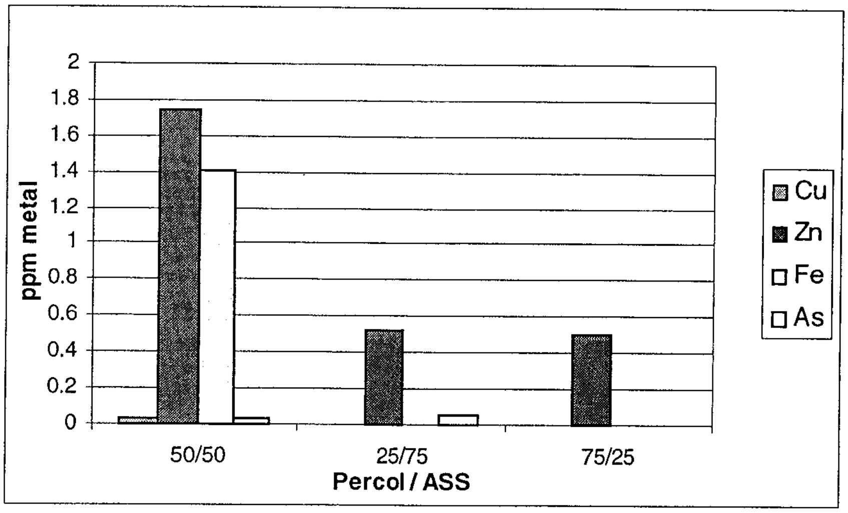

Figure 6.3a: Leachate from LEP test, 24 hours at pH 5, for the three combination tests.

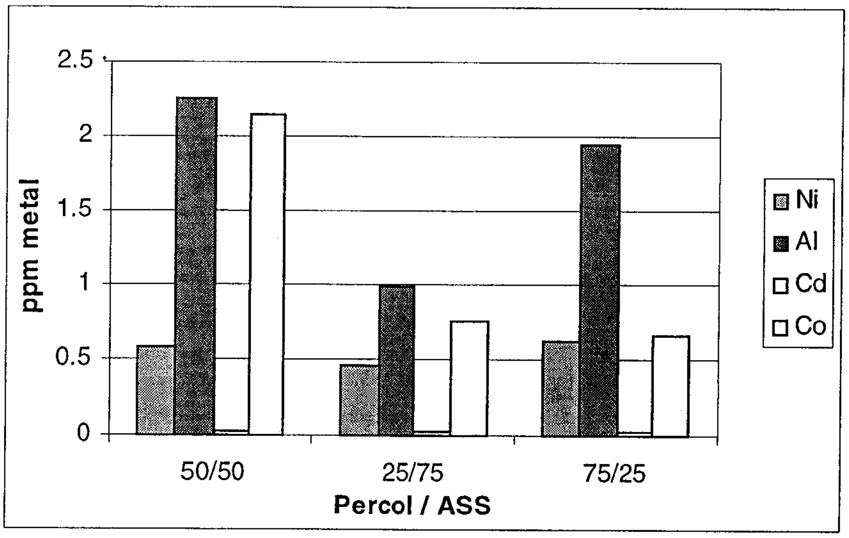

Figure 6.3b: Leachate from LEP test, 24 hours at pH 5, for the three combination tests.

Table 6.3: Comparison of leachates from LEP test with Doyon water samples and activated silica sol dosages.

Metal (ppm) in leachate	25P/75ASS 0,075 g SiO2/g Fe	Doyon 0,12 g SiO2/g Fe	Doyon 0,03 g SiO2/g Fe
Cu	0	1.04	0.741
Zn	0.53	5.52	5.03
Fe	0	0	0
Ni	0.46	1.55	2.01
Al	0.982	11.2	7
Cd	0.022	0.034	0.039

6.3.4 Conclusions

The settling characteristics of the sludge deteriorated with the combination of Percol and activated silica sol; however, the chemical stability of the sludge was improved slightly. Since it was possible to obtain stable sludge and good settling characteristics with only activated silica sol as the flocculant, the chemical stability improvement achieved with the combination of both flocculants was not enough to compensate for the loss in settling properties. Dosages of activated silica sol sufficient to show an increase in chemical stability over Percol could still provide settling of the sludge comparable to that with Percol.

6.4 Sludge recycling tests

6.4.1 Introduction

The major objective of these tests was to verify if the difference in chemical stability observed in single cycle tests with activated silica sol is enhanced or reduced when the sludge is recycled. A secondary objective was to compare the sludge density after recycle with Percol and activated silica sol. Four cycles were used. Batch settling tests were performed, and the supernatant decanted and the sludge introduced to the next cycle. The dosages of flocculant were $3\text{x}10^{-4}$ g Percol/g metal and 0.1 g SiO_2/g Fe. Standard leaching tests were performed on the sludge.

6.4.2 Sludge density

The density measurements were prone to errors as the decantation, being based on the visual appearance of the sludge, introduced inconsistencies. The sludge was allowed to settle for 40 minutes. The results are presented in Table 6.4. Four repetitions of each test were conducted for statistical analysis.

A t-test at the 95% confidence interval gave the following ranges in mean density:

Activated silica sol:	2.55% - 5.61% solids
Percol:	4.68% - 5.38% solids

The ranges overlap, therefore the two flocculants provide similar sludge densities when the sludge is recycled four times.

Table 6.4: Sludge density after 4 cycles

Flocculant	Test	Density (% solid)
ASS	R1	4.98
ASS	R2	4.84
ASS	R3	3.18
ASS	R4	3.33
Average ASS		4.08 S = 0.959
Percol	R5	5.09
Percol	R6	4.35
Percol	R7	5.27
Percol	R8	5.39
Average Percol		5.03 S = 0.218

6.4.3 Sludge chemical stability

The eight individual leachates obtained from the leaching tests were well below the regulation limits. The metal concentration in the leachate was averaged for the 4 repetitions of the same test and the results are presented in Table 6.5. Both Percol and activated silica sol behaved well, but Percol showed less variation between individual tests than activated silica sol.

All the tests had a lower metal leachate concentration than most previous single cycle tests, and most required more acid to decrease pH to 5. Table 6.6 compares single cycle leachates to four cycle leachates (same acid water, same flocculant dosage). The stabilizing effect of recycle was thus observed with both Percol and activated silica sol, and the stability difference between Percol and activated silica sol obtained with single cycle tests is no longer evident after 4 cycles. Several auxiliary experiments were conducted to try to explain this disappearance of the benefits of activated silica sol.

Table 6.5: Metal concentration in the leachate (ppm) after 4 cycles of sludge recycling

Metal	**Percol**	**silica**
Cu	0	0
Zn	0.237	0.487
Fe	0	0
Al	1.063	4.874
Ni	0.22	0.386
Cd	0.014	0.019
Pb	0	0
Mg	938	1066
Ca	2556	2095
Si	7.86	16.98
Mn	9.88	12.98
Na	3.67	9.24
Cr	0	0
As	0	0

Table 6.6: Comparison of leachate between single cycle and four cycles of sludge recycling

Metal	Percol 1 cycle	Percol 4 cycles	silica 1 cycle	silica 4 cycles
Cu	0.533	0	0	0
Zn	2.343	0.237	0.822	0.487
Fe	0	0	0	0
Al	45.8	1.063	18.6	4.874
Ni	1.41	0.22	0.984	0.386
Cd	0.028	0.014	0	0.019
Pb	0	0	0	0
Mg	1446	938	1915	1066
Ca	2097	2556	1753	2095
Si	24.4	7.86	20.9	16.98
Mn	31.9	9.88	33.6	12.98
Na	7.26	3.67	13.3	9.24
Cr	0	0	0	0
As	0.01	0	0	0

6.4.3.1 Lime overdosage

A complication may be the build-up of lime in the procedure adopted which masks the effect of activated silica sol. A clue is the added acid required to decrease the pH for Percol as well as activated silica sol. In a continuous process lime addition would probably be less.

Recognizing this, the amount of fresh lime added at each cycle was reduced. Only enough lime to reach pH 9.7 was added, and less was needed with each additional cycle. The final (after 4 cycles) sludge pH was not higher than with single-cycle tests. A chemical analysis of the sludge proved that there was slightly more calcium in the recycled sludge (Table 6.7), while the other elements were present in similar amounts.

The neutralization potential (NP) can indicate the efficiency of the lime consumption. A low NP corresponds to a better lime utilization while a high NP reveals excess neutralizing components such as lime and carbonates (from carbon dioxide) [37]. The neutralization potential measurement procedure was adapted to the hydroxide sludge; the titration was considered complete when the pH stayed at 4.5 for more than an hour. The results are presented in Table 6.8. A higher NP was obtained with activated silica sol meaning that the sludge has a better neutralizing capacity over Percol sludge. However, for both types of sludge the recycled sludge has a lower NP compared with single cycle. This was also observed by Zinck [37] and explained as a better lime utilization with the sludge recycling process.

From the chemical analysis and neutralization potential measurements there is no evidence that lime overdosage explains the disappearance of the effect of activated silica sol on recycled sludge. It would appear that lime was used more efficiently with the sludge recycling process.

Table 6.7: Calcium content of the sludge

	wt% Ca
Recycled Percol	26.0
Single-cycle Percol	25.1
Recycled ASS	27.9
Single-cycle ASS	23.0

Table 6.8: Neutralization potential of the sludge

	NP (kg $CaCO_3$/t)
Recycled Percol	664.6
Single-cycle Percol	700.8
Recycled ASS	720.6
Single-cycle ASS	837.5

6.4.3.2 Particle size and crystallography

The literature [37, 38] mentions that sludge produced through recycling has smaller particles and a narrower size distribution. In the laboratory experiment, only four cycles were simulated, but particle size analysis revealed a slightly narrower size distribution for the recycled sludge. Again it indicates that lime efficiency was increased with sludge recycling and overdosage is not an issue.

The dried sludge was observed under the scanning electron microscope. Previous experiments by Payette et al. [38] showed that recycled sludge exhibits a more crystalline structure than single-cycle sludge. Metals trapped in a crystal are more difficult to leach, thus are less likely to appear in the leachate.

The recycled sludge had larger and more numerous crystals than single-cycle sludge. It was postulated that the particles had more favorable conditions to crystallize and grow with the recycling and re-precipitation. Figures 6.4a and 6.4b present micrographs of single-cycle and four-cycle sludge, respectively. In the case of recycled sludge, crystals became visible at a magnification of 400x to 800x, while single-cycle sludge required a magnification of 2000x. In both cases, the composition of the crystals remained the same, i.e. a compound made mainly of calcium, sulphur, aluminum and iron.

There were no obvious structural differences between sludge precipitated with Percol or with activated silica sol. Both exhibited the same crystal size and abundance in either cases (recycled and single-cycle). The difference in crystallography between single-cycle and recycled sludge probably accounts for the increased stability for both Percol and activated silica sol when the sludge is recycled. The enhanced crystallinity due to recycle was a more powerful stabilizing factor than the addition of activated silica sol in single cycle test, at least in this study.

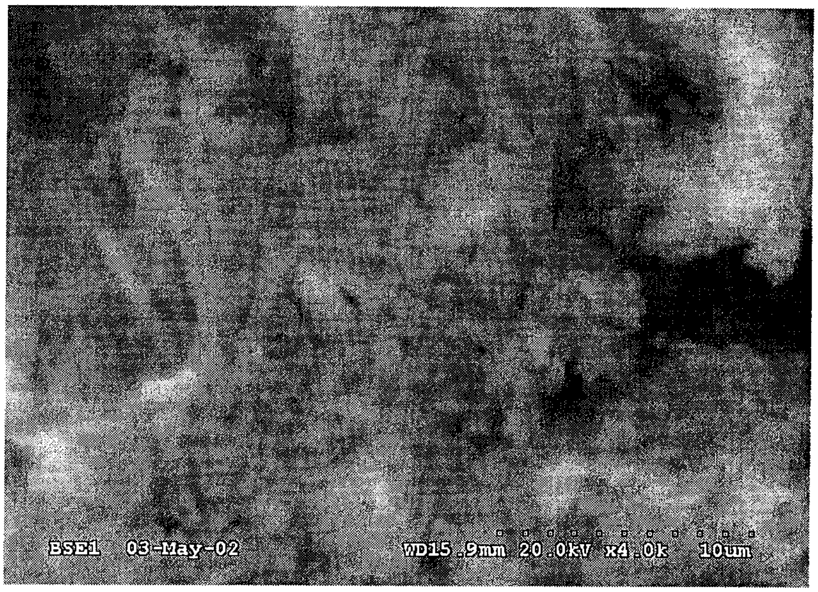

Figure 6.4a: Photograph of single-cycle sludge precipitated with activated silica sol, magnification 4000x.

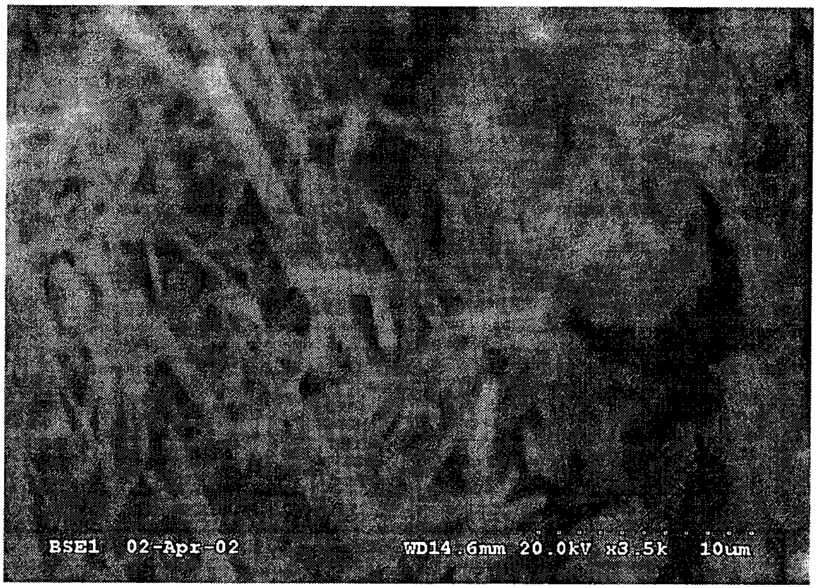

Figure 6.4b: Photograph of recycled sludge precipitated with Percol, magnification 3500x.

6.4.4 Conclusions

From a statistical perspective, similar sludge densities were obtained after 4 settling cycles using Percol and activated silica sol as the flocculant. The sludge performed well under the leaching test, all the sludges being compliant to the regulation limits. The improvement in sludge stability observed with activated silica sol over Percol in single cycle tests is not present after 4 cycles. Lime overdosage was discounted as an explanation following neutralization potential measurements and particle size analysis. What was observed was that recycled sludge had larger and more numerous crystals for both Percol and activated silica sol sludge. The crystals retained the metals better than when in amorphous form, thus increasing sludge stability.

Chapter 7: Summary

7.1 Conclusions

Activated silica sol is a non-toxic agent that is used as a flocculant and for heavy metal control in the treatment of effluents. In the present study, activated silica sol was used in conjunction with lime to produce a clear mine effluent discharge and a chemically stable sludge. The conclusions obtained from the settling and leaching tests are summarized below.

7.1.1 Settling tests

- Activated silica sol can provide similar settling characteristics as Percol when used in low dosages (below 0.1 g SiO_2/g Fe).
- Low dosages of activated silica sol yield a more compact sludge.
- The settling rate is not a function of activated silica sol dosage alone; it is influenced by the water chemistry.
- The settling rate decreases with an increase in magnesium concentration in the mine water, especially when activated silica sol is used as the flocculant.
- A minimum iron concentration in the water is required apparently to promote activated silica sol to polymerize and flocculate the fine particles.
- A higher ferric / ferrous ratio in the water is desirable for a high settling rate.

7.1.2 Leaching tests

- A high activated silica sol dosage (above 0.05 g SiO_2/g Fe) is beneficial to the sludge chemical stability.
- The action of activated silica sol is two-fold: it creates stable adsorption bonds between silica and metal compounds, and the buffer effect keeps the sludge pH high.
- The minimum iron requirement mentioned in the settling section is still applicable; without good bonding between the silica and solid particles the sludge stability improvements are not present.
- A dosage of 0.1 g SiO_2/g Fe activated silica sol yielded good settling characteristics and improved sludge chemical stability.
- Leaching tests with a weak leachant yielded regulation compliant effluents for both sludges (Percol and activated silica sol).
- Observations suggested that the sludge precipitated with activated silica sol would remain chemically stable for a longer period of time than sludge precipitated with Percol.

7.1.3 Complementary tests

- Heating the sludge precipitated with activated silica sol does not improve its chemical stability.
- There is no improvement in the settling characteristics of the sludge with the combination of Percol and activated silica sol. The chemical stability is improved slightly.

- The chemical stability improvement achieved with the combination of Percol and activated silica sol is not high enough to compensate for the loss in settling properties. Activated silica sol works better when used alone.
- The densities obtained using Percol or activated silica sol after sludge recycling over four cycles are similar.
- The recycled sludge is more stable than single-cycle sludge for both Percol and activated silica sol. The improvement in sludge stability observed with activated silica sol over Percol in single-cycle tests is not present after four cycles.

7.2 Suggestions for further work

- High-density sludge: Tests should be conducted to understand the effect of activated silica sol with the high-density sludge (HDS) process. A laboratory scale HDS could be used before moving on to pilot scale. Comparison with a standard flocculant would quantify the benefits in terms of sludge chemical stability.
- Dosage optimisation: Activated silica sol should be tested on pilot scale to optimise the dosage for maximum settling and stability benefits. An economic analysis could be conducted to compare the costs of activated silica sol with a standard flocculant.

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Appendix 1

Chemical analyses of the collected mine effluents

Table A1: Chemical analyses of the collected mine effluents (concentrations in ppm)

Test #	Source	Date*	As	Ca	Cu	Fe	Zn	Mn	Pb	Ni	Al	Cd	Si	Mg	Co	Cr
D1 - D4	Doyon	14-02-01	0	372	4,05	402	1,84	16,22	0	0,48	128	0,10	19,5	173	0,80	0,18
L1 - L5	Laronde	26-02-01	0	353	3,11	3,55	16,63	5,70	0	0,08	1,93	0,05	12	30	0,07	0
W1 - W4	Waite Amulet	12-03-01	0	227	0,72	238	4,37	4,89	0	0,02	14	0,06	20,4	95	0,05	0,06
N1 - N5	Mine N	19-04-01	0	441	3,24	799	18,88	17,24	0	0,05	39,6	0,16	23,5	173	0,20	0,07
T1 - T9	Mine N	16-05-01	0	308	14,69	297	47,35	11,53	0	0,15	76,7	0,16	20,6	108	0,50	0,03
T10 - T12	Mine N	16-05-01	0	370	15,82	500	52,14	14,29	0	0,15	82,4	0,21	24,1	142	0,50	0,06
DM1-DM3	Doyon	13-09-01	0	383	6,20	790	2,52	25,20	0	0,83	327	0,16	30,4	340	1,43	0,26
CHP-CHS	Doyon	13-09-01	0	383	6,20	790	2,52	25,20	0	0,83	327	0,16	30,4	340	1,43	0,26
R1 - R8	Doyon	21-11-01	0	259	9,61	2786	5,19	47,65	0	1,96	1041	0,63	43,7	944	3,08	2,06
C1 - C8	Doyon	21-11-01	0	259	9,61	2786	5,19	47,65	0	1,96	1041	0,63	43,7	944	3,08	2,06

*: date analysed

Appendix 2

Tables from Directive-019 [9]

Table A2-1: Maximum concentrations (in ppm) measured at the final effluent

Parameter	Max concentration (monthly average)
Arsenic (total)	0.5
Copper (total)	0.3[1]
Nickel (total)	0.5[1]
Lead (total)	0.2[1]
Zinc (total)	0.5[1]
Iron (total)	3
Cyanide (total)	1.5
Cyanide (free)	0.1
Solids in suspension	25
Hydrocarbons	15
pH	6.5 to 9.5
No acute toxicity at final effluent	

[1]: The sum of Cu, Zn, Pb, Ni cannot exceed 1 ppm

Table A2-2: Sampling frequency for the different parameters

Continuous	Weekly	Variable (Table A2-3)	Yearly
pH	Conductivity	Arsenic	Aluminum
Flowrate	Solids in suspension	Copper	Cadmium
	Temperature	Nickel	Chrome
		Lead	Cobalt
		Zinc	Manganese
		Iron	Mercury
		Cyanide (total)	Hardness
		Cyanide (free)	Ammonia
		Hydrocarbons	Nitrates
			Nitrites
			Alkalinity
			Dissolved inorganic carbon

Continuous	Weekly	Variable (Table A2-3)	Yearly
			Dissolved organic carbon
			Phosphorus
			Sulphates
			Sulphurs
			Thiosulphates
			Cyanates
			Thiocyanates
			Biotesting of Daphnia
			Biotesting by Microtox

+ biotesting of rainbow trout every three months

Table A2-3: Sampling frequency of variable parameters

Parameter	Weekly if monthly average > or =	Every two weeks if monthly average > or =	Monthly if monthly average > or =	Every six months if monthly average > or =
Arsenic	0.50	0.20	0.10	0.10
Copper	0.30	0.05	0.025	0.025
Nickel	0.50	0.30	0.10	0.10
Lead	0.20	0.10	0.05	0.05
Zinc	0.50	0.20	0.10	0.10
Iron	3.00	2.00	1.00	1.00
Cyanide (total)	1.50	0.80	0.30	0.30
Cyanide (free)	0.10	0.05	0.02	0.02
Hydrocarbons	--	--	Presence	Absence