

IRON CONTROL IN HYDROMETALLURGY: THE POSITIVE SIDE OF THE COIN

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ABSTRACT

During the hydrometallurgical processing of the major base metals Cu, Zn, Ni and Co, the presence of iron is normally a serious complication, and iron separation from the pay metals usually constitutes one of the main challenges for the metallurgist. There are many instances, however, where the presence of iron is beneficial, or is even required. Two cases are presented where iron is required during the processing of base metals. The first example deals with the use of ferric sulphate to oxidize sulphides, more particularly copper and zinc sulphides, under atmospheric conditions. The results presented confirm that ferric ion leaching is efficient, particularly when the oxidant is regenerated during the process. The second case is the use of iron to solubilise refractory cobalt oxide minerals; examples, including pilot plant results, are presented for various ores from Africa and Central America. In both cases, this paper reviews the basic concepts involved and provides details of their application.

INTRODUCTION

Iron is the fourth most abundant element in the earth's crust, and it is no surprise that the common minerals of the major base metals (Cu, Zn, Ni and Co) include iron in their structure. Examples are chalcopyrite (CuFeS_2) and bornite (Cu_5FeS_4) for copper and pentlandite ($\text{Fe,Ni}_9\text{S}_8$) for nickel. Low-iron sphalerite (ZnS) deposits are not common, and the typical zinc sulphide deposits usually contain minerals of the sphalerite-marmatite ($(\text{Zn,Fe})\text{S}$) family, with variable iron concentrations that can reach that of marmatite ($\text{Zn}_x\text{Fe}_y\text{S}$), with a y value of 17% (w/w).

In addition to the iron-base metal mineralogical associations, the concentration methods (mostly flotation) that are used to produce the various base metal concentrates are not perfect; very common contaminants of these concentrates are iron sulphides, such as pyrite (FeS_2) and pyrrhotite (FeS). The production of pure metals from typical base metal concentrates will therefore require one or more steps of selective iron removal. If the base metal concentrates are treated by pyrometallurgical techniques, then the iron is relatively easily separated from the base metal in the smelter and reports as a slag. A good example is provided by the smelting of chalcopyrite concentrates.

The situation is far more complicated when treating base metal concentrates by hydrometallurgical techniques. The iron separation step is normally more complex, to the point that, for zinc for example, the method of removing the iron dominates the whole purification process, and the various processes are characterized by the type of iron compound formed during the purification stage (jarosite, goethite, hematite, para-goethite).

The recently developed processes for the acid leaching of nickel laterites can, for example, be compared based on the options for handling the iron. The high temperature (up to 280°C) processes take advantage of the leaching conditions that favour iron hydrolysis to rapidly precipitate the iron and release the acid. The low temperature processes on the other hand do not use autoclaves and operate under conditions that do not favour iron hydrolysis during the leach; efforts have then to be made downstream to handle the relatively concentrated iron solutions and recover the acid and nickel from them.

In another example, the hydrometallurgical treatment of copper developed significantly after solvent extractants selective for copper over iron were commercialized. Hopes for a similar success were also briefly entertained for zinc, when an iron-selective zinc

extractant was developed [1], only to see those hopes dashed a few years later when it was realized that the extractant had stability issues.

As a consequence, most hydrometallurgists have to make appreciable efforts in dealing with iron separation issues in their circuits. There are, however, many cases where the hydrometallurgist can make use of iron to help solve some of the processing issues.

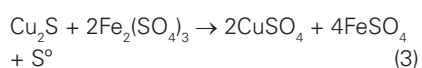
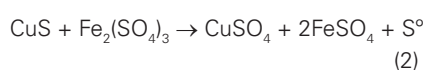
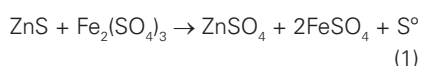
The use of metallic iron as a cementing agent has been long known. The use of dissolved iron to control and/or stabilize arsenic has been the topic of much research in recent years. Research is continuing to try to elucidate the various mechanisms involved for the different situations, in particular depending on the arsenic concentration. Despite some remaining fundamental uncertainties, the process is well established industrially.

The use of the ferrous/ferric couple was suggested several years ago [2] to provide an alternate anode reaction to the conventional evolution of oxygen during copper electrowinning. Under this scenario, the electrolyte contains significantly larger concentrations of iron than usual; the ferrous iron oxidation at the anode provides the electron-donor reaction to balance the cathodic electron-receptor reaction of copper metal deposition. To promote this alternate anode reaction, a more reactive anodic material has to be used (DSA anode). This process is still being evaluated, and has been recently piloted by a leading copper producer [3].

This paper details two other positive uses of iron in hydrometallurgy. The first case describes the use of iron as an oxidant to leach metal sulphides, in particular copper and zinc sulphides. The second case describes the use of iron as a reductant for the leaching of refractory cobalt oxides.

IRON AS AN OXIDANT TO LEACH METAL SULPHIDES

The role of ferric iron as an oxidant during the acidic leaching of metal sulphides has been known for decades [4]. The chemical reaction can be written for the sulphate system as:

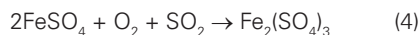


As indicated above, elemental sulphur is formed in all cases, and the physical

nature of the sulphur layer has a significant impact on the kinetics of the reaction. If the sulphur forms an adherent compact layer, the kinetics will be controlled by the diffusion of reactants and products through that layer, and slow kinetics will result. On the other hand, if the sulphur is not adherent or is porous, then diffusion through it is not rate controlling, and the overall kinetics are greatly improved.

For practical reasons, it is normally necessary to re-generate the ferric iron to avoid having to use excessive concentrations of iron in solution. The regeneration of the ferric iron can be effected by various means. Bacterial oxidation (for example using *Thiobacillus ferro-oxidans*) has been known and is applied widely. Oxidation of ferrous iron using oxygen or air is relatively slow in acidic media, unless it is conducted above atmospheric pressure. Better oxidation kinetics are obtained when using SO₂/O₂ mixtures [5,6,7].

The chemical reaction for the regeneration of ferric ion can be described by Reaction 4 for sulphate media:



SECONDARY COPPER SULPHIDES

The results for the treatment of two copper samples will be discussed here. The chemical analyses of the two

samples are presented in Table 1.

Table 1 – Chemical analyses of the two samples tested

Sample	1	2
%Cu	37.7	5.91
%Fe	17.1	11.2
%S ²⁻	29.2	8.6
Origin	USA	Asia

Sample 1 was a flotation concentrate composed primarily of sulphides (covellite, chalcocite/digenite, pyrite) with little gangue (~6%). Sample 2 was an ore containing copper mostly as covellite, with minor chalcopyrite and enargite.

The advantage of regenerating the ferric ion during the leach is shown in Figure 1.

If the ferric ion is not regenerated, copper dissolution is limited to about 38%. When oxygen is sparged during the leach (all other parameters being kept constant) the copper dissolution reaction progresses slowly, reaches 62% after 6 hours, and is clearly not completed. If instead of using pure oxygen, SO₂/O₂ mixtures are used, and in particular a mixture 5% SO₂ - 95% O (v/v), then the copper dissolution reaction proceeds faster, reaching 88% after 6 hours, and still continuing thereafter.

The same conclusions can be drawn

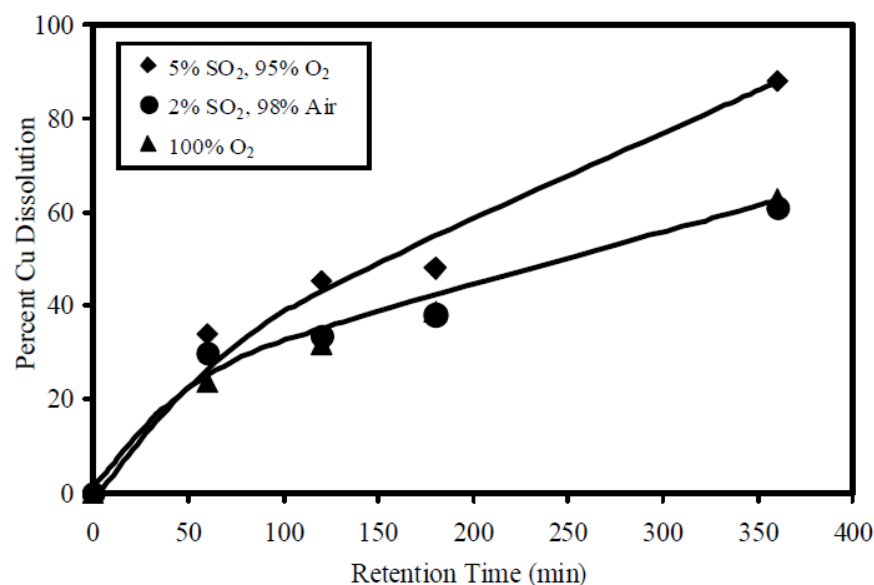


Figure 1 – Regeneration of ferric ion using oxygen or SO₂/O₂ mixtures. Temperature: 80°C, P₈₀ = 55 microns, 4% solids, 10 g/L Fe initial. Sample 1

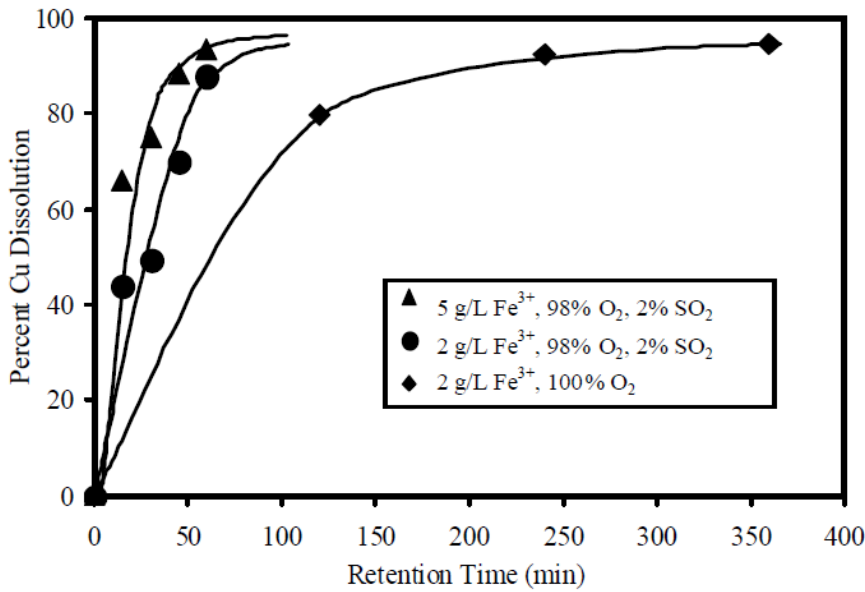


Figure 2 – Regeneration of ferric ion using oxygen or SO₂/O₂ mixtures. Temperature: 80°C, P₈₀ ~100 microns, 10% solids, sample 2

when examining the leaching of sample 2, as shown in Figure 2.

The results indicate much faster kinetics of copper dissolution with ferric sulphate, when the regeneration of the oxidant is carried out using SO₂/O₂ mixtures (2% SO₂ (v/v)), all other parameters being kept constant, as compared to the use of pure oxygen.

ZINC SULPHIDE

Most of the world’s zinc production is derived from treating sphalerite ((Zn,Fe)S) concentrates via the roast-leach-electrowinning (RLE) process. In this well established process, the zinc sulphide is oxidized in a roaster prior to being subjected to a sulphuric acid leach. However, over the years, several processes have been developed to leach zinc directly from the sphalerite; i.e., to oxidize and leach the sphalerite in the same reactor. Two direct leaching processes have reached commercial application, as indicated in Table 2.

In both the pressure leaching and atmospheric leaching of sphalerite, the main oxidant is ferric sulphate. Regeneration of the ferric ion is accomplished by oxygen under pressure for the pressure leaching option, and by oxygen at atmospheric pressure for the atmospheric leaching process which requires up to 24 hours retention time to reach completion.

The sphalerite used in that program was

a low-grade bulk concentrate assaying 32% Zn, the remainder being mostly pyrite. All other conditions being kept constant, the use of SO₂/O₂ mixtures improves the ferric ion regeneration to the extent of achieving ~60% extraction in 4 hours, as compared to ~30% with the use of pure oxygen. As indicated earlier, the regenerated ferric sulphate leaching of copper or zinc sulphides proceeds via a two-step process: the oxidation of the sulphide, leaching of the metal with the production of ferrous sulphate, followed by the regeneration of the ferric sulphate. Each of these reactions follows a rate equation with a specific rate constant. Optimum conditions (in particular temperature) for one reaction might not be optimum for the other, and there could be advantages in carrying out the two reactions in separate vessels (ex-situ), such as illustrated in Figure 4.

An example of the application of the ex-situ regeneration is presented in Figure 5 for a

Figure 3 – Comparison of O₂ and SO₂/O₂ mixtures (2% SO₂ (v/v)) to regenerate ferric sulphate solutions during sphalerite leaching at 70°C and 10 g/L Fe³⁺ initial concentration

Operator	Country	Plant	Capacity (kt Zn/y)	Start-up Year
Pressure leaching				
Teck Cominco	Canada	Trail	60	1981
Falconbridge	Canada	Kidd Creek	60	1983
Hudson Bay	Canada	Flin Flon	100	1993
Kazakhmys Copper Corp.	Kazakhstan	Balkhash	100	2003
			320	
Atmospheric Leaching				
Korea Zinc Company	South Korea	Onsan	200	1994
New Boliden	Finland	Kokkola I	50	1998
New Boliden	Finland	Kokkola II	50	2001
New Boliden	Norway	Odda	50	2004
			350	

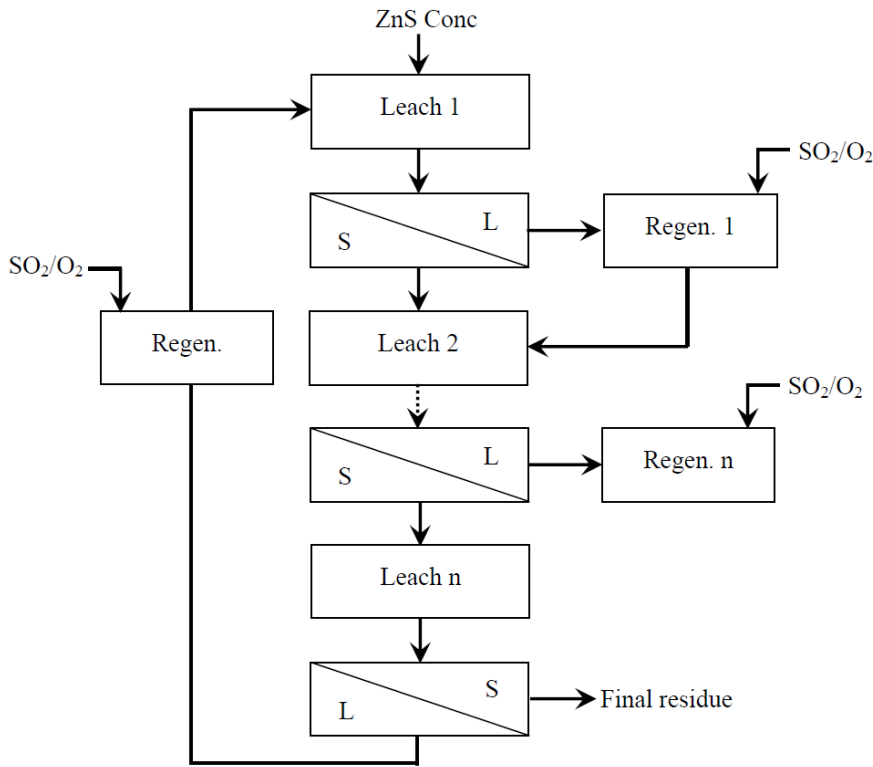


Figure 4 – Schematic flowsheet for the regenerated ferric sulphate leaching of sphalerite (Ex-situ)

A second leach stage then begins, and the cycle is repeated.

IRON AS A REDUCTANT TO LEACH REFRACTORY COBALT MINERALS

In the Central African Copper Belt (Zambia and Democratic Republic of Congo (ex Zaire)), cobalt is found primarily as carrollite (CuCo_2S_4) in the sulphide zone, and as heterogenite (CoOOH) in the oxide zone, as well as in a weathered compound named "cobalt wad", a soft manganese oxide of low density. This cobalt oxide-rich layer, named BOMZ (Black Ore Mineralized Zone) is characterized by its black MnO_2 component. Sea and land nodules also contain a similar association between manganese and cobalt in wad [9]. Manganese and cobalt (and nickel) are also found associated in laterites [10,11,12,13], in minerals of the asbolan-asbolite group of general formula $(\text{Co}, \text{Ni})_{1-y}(\text{MnO}_2)_{2-x}\text{OH}_{2-2x-2y}$ [14].

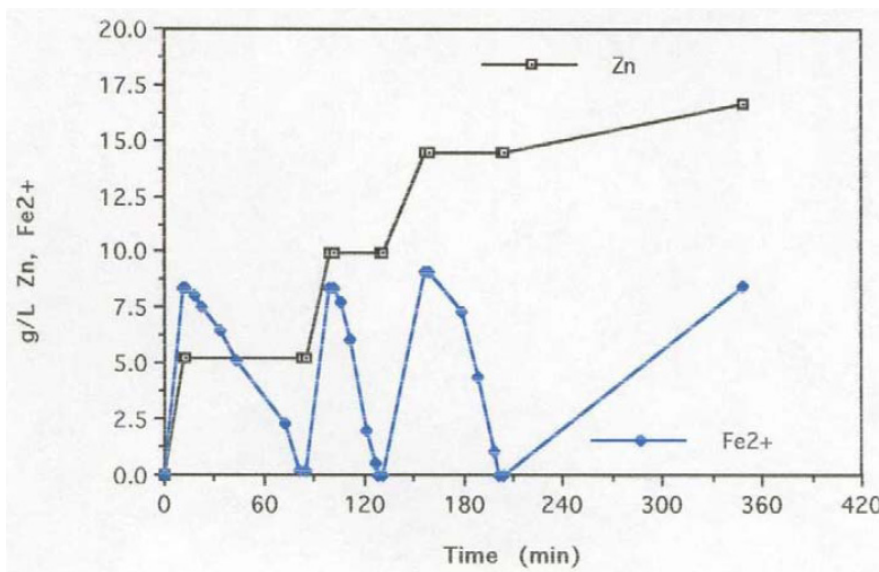


Figure 5 – Ex-situ regeneration of ferric sulphate using SO_2/O_2 mixtures (2% SO_2 (v/v)) at 70°C; 8 g/L Fe_3+ initial concentration; $P_{80} \sim 15 \mu\text{m}$

Canadian concentrate assaying 60.75% Zn, 1.13% Pb, 0.40% Fe and 28.3% S.

The results indicate that under the conditions of the test, four stages of total retention time (leaching + regeneration, but not thickening) of 350 minutes would be sufficient to complete the leaching (Zn extraction >95%). One curve represents the cumulative concentration of zinc in the

leach solution that increases in steps of about 5 g/L Zn, followed by plateaus corresponding to the regeneration of the ferric sulphate. The second curve follows the concentration of ferrous sulphate: at the start, all the iron is in the ferric state ($\text{Fe}^{2+} = 0 \text{ g/L}$), during leaching, ferric ion is consumed and the concentration of ferrous ions increases to the maximum (~8 g/L Fe^{2+}). The ferric ion is then regenerated (ferrous decreases to 0 g/L).

Manganese dioxide can be dissolved in acidic reducing conditions, the reducing conditions being created chemically by SO_2 (either gaseous, or aqueous H_2SO_3 or similar compounds Na_2SO_3 , $\text{Na}_2\text{S}_2\text{O}_5$, etc.) or even bacterially [15,16,17,18]. Because of the close mineralogical association between the manganese and cobalt, it is expected that acidic reductive SO_2 leaching would also dissolve the cobalt from Co-Mn wad or nodules, and this has been proven to be the case. In the work described here, a few cobalt samples were tested, as shown in Table 3.

Ore types A, B, C were of African origin and exemplify copper-cobalt oxide ores without manganese. Ore type D was from Central America, and exemplifies a copper-cobalt oxide ore with manganese, whereas ore type E was from North Africa and exemplifies a nickel-cobalt laterite, with manganese.

REDUCING LEACHING USING SO_2

Samples of ore type A, ground to a P_{80} of 80 microns, were leached with agitation at 33°C. During the leach, the pH was maintained at ~1.9 using sulphuric acid. The results of the leach are presented in Figure 6.

Table 3 – Chemical analyses of cobalt ores and concentrates used in the study

	A	B	C	D	E
%Cu	9.9	4.8	5.1	0.43	<0.01
%Co	1.8	0.43	0.43	0.07	0.75
%Fe	1.8	1.8	1.8	7.94	36
%Mn	<0.05	<0.05	<0.05	4.49	-
%Ni	-	<0.003	<0.003	0.01	0.8

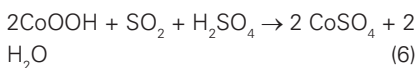
As can be seen from the graphs, copper dissolution in acidic solutions (pH ~1.9) was excellent and reached 95% in 45 minutes. Cobalt dissolution, on the other hand, was limited to less than 10% even after 2 hours.

When the same ore was treated under exactly the same conditions, but with sparging gaseous SO₂ (for a total of 80 kg SO₂/t ore), after 120 minutes, the copper and cobalt extractions were 97.6% and 94.7%, respectively.

The reduction of MnO₂ with SO₂ occurs according to the reaction:



Similarly, the reduction of heterogenite likely occurs according to the reaction:



As expected, the use of SO₂ results in excellent cobalt dissolution even from Co-Mn ores. Figure 7 illustrates the extractions of cobalt and manganese from ore type E. In this particular case, SO₂ was added as sodium metabisulphite Na₂S₂O₅.

Sulphur dioxide is a very common reductant; it is effective and relatively inexpensive although it is subject to high price surges. The use of SO₂ presents several major drawbacks. The first drawback relates to environmental and safety risks associated with gaseous SO₂ emissions, even when using SO₂ as sulphurous acid. To minimize those risks, SO₂ could be used as sulphite (Na₂SO₃) or metabisulphite (Na₂S₂O₅). However, its efficiency is then reduced, and it introduces a counter ion (i.e., Na+) into the system that could build up beyond control. These emission

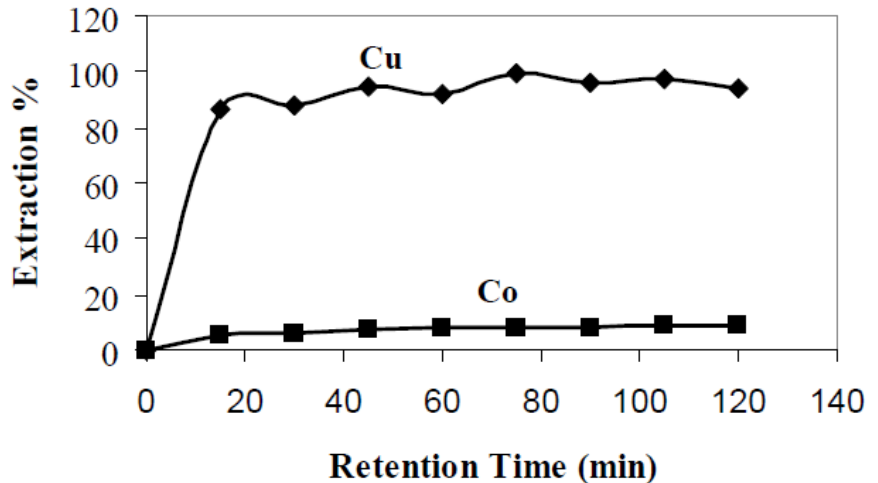


Figure 6 – Kinetics of copper and cobalt dissolution from ore type A when using only sulphuric acid: pH ~1.9; temperature = 33°C; P₈₀ = 80 microns

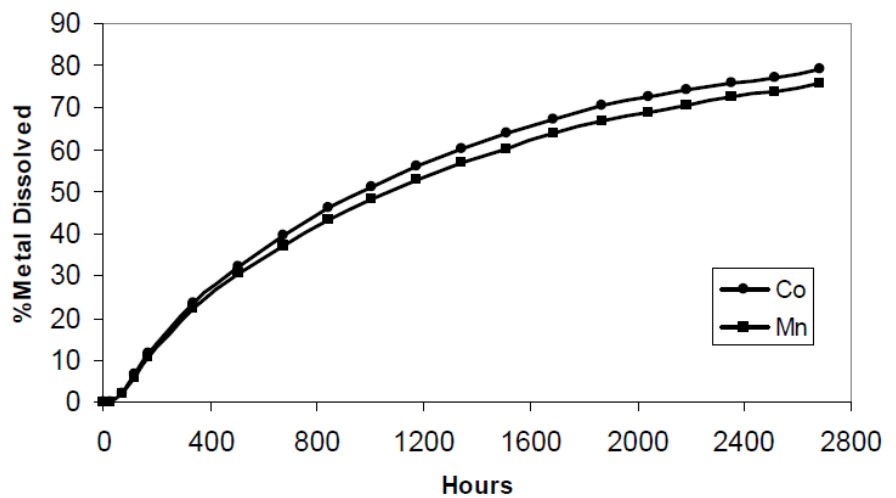
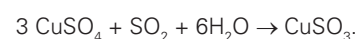
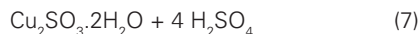


Figure 7 – Kinetics of Co and Mn dissolution from ore type E in a column leach

risks are quite serious if heap or vat leaching operations are considered. The second drawback relates to the lower gas mass transfer efficiency in a pulp as compared to a liquid. This lower efficiency translates into a higher reagent consumption. The third drawback is metallurgical in nature and is detailed in the following paragraphs. Figure 8 illustrates the effect of SO₂ additions on copper and cobalt extractions from ore

type A, all other conditions (temperature, acidity, grind size, retention time) being kept the same. The positive effect of SO₂ additions on cobalt extraction is confirmed, but there is also a significant drop in copper extraction at the higher SO₂ additions. This is likely due to the precipitation of Le Chevreult's salt, according to the reaction:



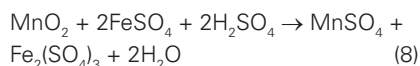


From a metallurgical point of view, it is a very dangerous situation when an excess of reagent could lead to such a significant loss of metal recovery. As a consequence of these serious disadvantages associated with the use of SO₂ as a reductant, an alternative reductant (non-SO₂ based) would be preferred.

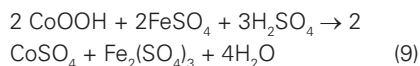
REDUCTIVE LEACHING USING FeSO₄

The use of ferrous sulphate FeSO₄ as an alternative to SO₂ for the leaching of manganese oxide ores has been suggested [19,20,21].

The reduction of manganese with ferrous sulphate occurs according to the reaction:



By analogy, the idea came to test the use of ferrous sulphate on oxidic cobalt ores, according to the assumed reaction:



The validation of the concept is presented in Figure 9, where ore type A was used. The results in Figure 9 indicate two significant features: first, ferrous sulphate can indeed efficiently reduce cobaltic hydroxide to the same extent as SO₂ (95-96% Co extraction) provided the appropriate amount is used. Secondly, excess additions of ferrous sulphate (for example 25 g/L Fe²⁺) have no negative impact on copper extraction.

The kinetics of ferrous sulphate reduction of cobaltic oxide are presented in Figure 10 for two ferrous sulphate concentrations in solution; 3 g/L and 9 g/L.

At 3 g/L Fe²⁺, the extraction reaches a plateau at ≤ 45 minutes, because of the depletion of the reducing agent. At 9 g/L Fe²⁺, the cobalt extraction reaches 80% in 90 minutes, and then continues to increase at a slower rate till it reaches 92% after 240 minutes. The shape of the curve indicates that a plateau has not yet been reached.

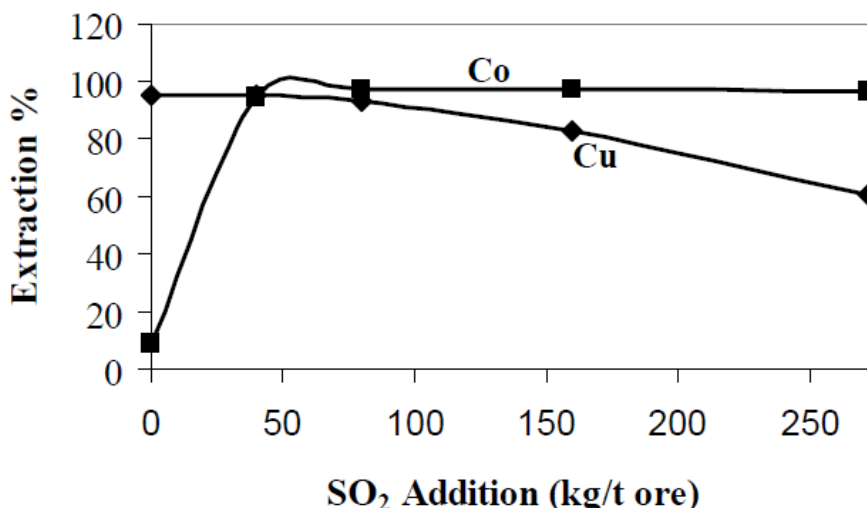


Figure 8 – Effect of SO₂ additions on Cu and Co extractions from ore type A. Temperature: 33°C; pH ~1.9; P₈₀ = 8 µm; retention time: 120 minutes

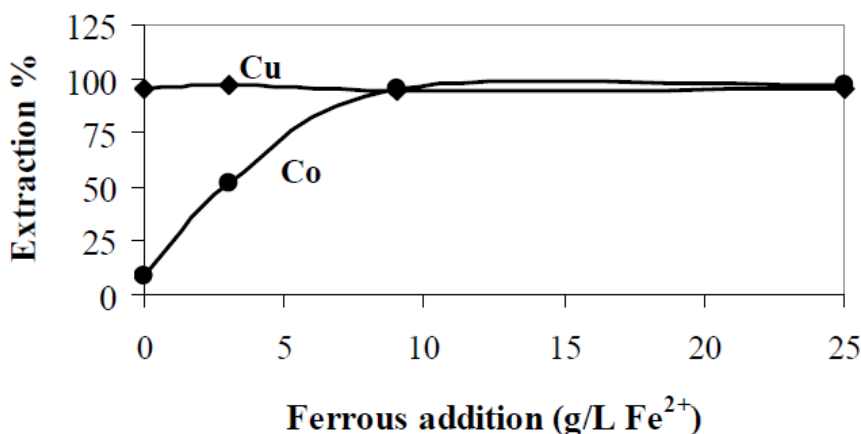


Figure 9 – Effect of ferrous sulphate additions on copper and cobalt extractions from ore type A. Temperature: 33°C; retention time: 240 minutes; pH ~1.9; 30% solids

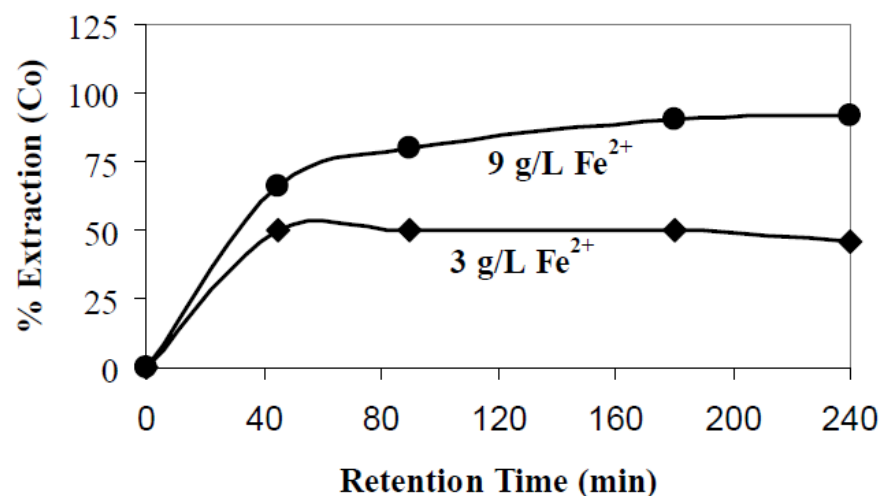


Figure 10 – Kinetics of cobalt extraction from ore type A. Temperature: 33°C; pH ~1.8; 30% solids (w/w); P₈₀ = 80 µm

APPLICATION TO OTHER COBALTIC OXIDE ORES

The results presented above have confirmed that ferrous sulphate could be effectively used on a cobaltic oxide ore (ore type A) containing copper but no manganese. Tests were carried out to examine whether the procedure could be used on other Cu-Co ores and, in particular, on Co-Mn ores. The kinetics of cobalt extraction from ore type B, using 5 g/L Fe²⁺, are presented in Figure 11.

Samples of ore types D and E (Co-Mn ores) were also agitation-leached, using ferrous sulphate as the reducing agent. The results obtained on ore type E were identical to those realized with SO₂. The results for ore type D are presented in Figure 12.

Without a reductant, under the conditions used, about 44% of the Mn and 58% of the Co are dissolved in the acid in 4 hours. Ferrous ion additions increase the Mn recovery to practical completion (97.5%), whereas the cobalt recovery is increased by 20%.

REGENERATION OF THE REDUCTANT

As shown in Reaction 8, the reduction of trivalent cobalt using ferrous sulphate generates ferric ions. If warranted, the regeneration of the ferrous sulphate can easily be accomplished by using SO₂.

A solution containing 12 g/L Co, 1.5 g/L Cu, 26 g/L acid and 6.8 g/L Fe³⁺ was used for the regeneration tests. This solution represents a raffinate obtained after the solvent extraction of copper from a Cu-Co leach solution. The regeneration tests were conducted by sparging variable flows of gaseous SO₂ through one litre of solution maintained at 33°C and mechanically agitated using a Rushton-type impeller rotated at 320 RPM. The extent of the conversion as a function of time is illustrated in Figure 13 for three SO₂ sparging rates: 0.035 L/min, 0.070 L/min and 0.100 L/min.

The reduction of ferric sulphate with SO₂ is rapid, and is completed in less than one hour at the higher flow rate. The

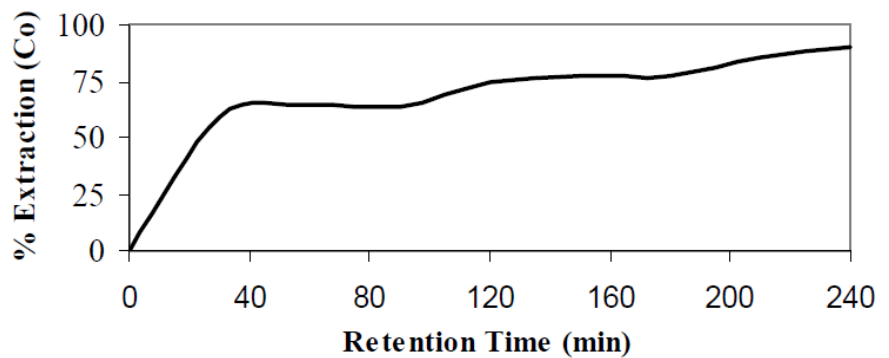


Figure 11 – Kinetics of cobalt extraction from ore type B using 5 g/L Fe²⁺ (initial). Temperature: 33°C; pH ~1.8; 30% solids (w/w); P₈₀ = 80 µm

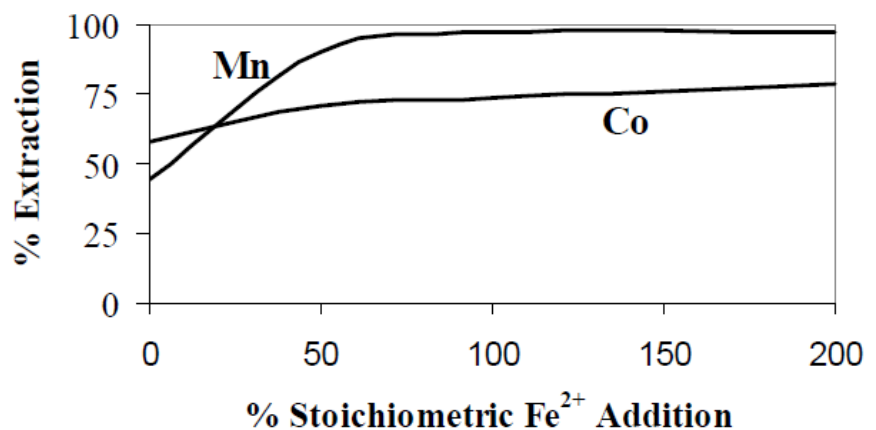


Figure 12 – Extraction of Co and Mn from ore type D as a function of the stoichiometric (Mn + Co) Fe²⁺ ion addition. Temperature at 50°C and pH ~1.5

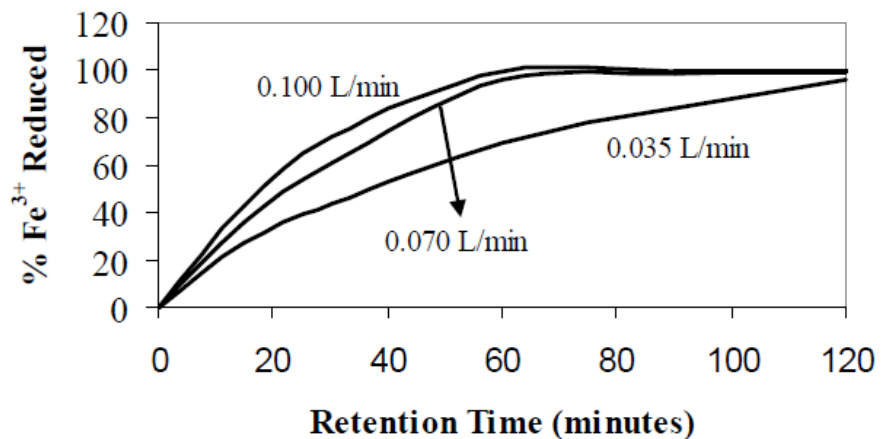
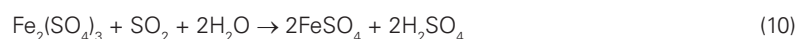


Figure 13 – Kinetics of ferric sulphate reduction with SO₂ for three sparging rates. Temperature: 33°C; RPM = 320; initial Fe³⁺: 6.8 g/L

reduction of ferric sulphate occurs according to the reaction:



The extent of the reaction is easily followed by monitoring the emf of the solution. It should be noted that the reaction produces 1 mole of acid per mole of ferric ion reduced. The reduction of ferric ion is carried out with no solids present, and, as a consequence, the mass transfer is better than for a pulp. Finally, the SO₂ addition is restricted to one reactor, and not to the leaching stage. Gaseous emissions from the leach reactor, in particular if it is a heap or vat leach reactor, are non-existent.

VAT LEACHING OF COBALTIC ORES USING FERROUS SULPHATE AS A REDUCTANT

The advantage of using ferrous sulphate as a reductant to solubilise cobaltic ore is best

demonstrated by examining the results of a column test carried out to simulate vat leaching of ore type C. For the test, 10 kilograms of minus ¼ inch (0.635 cm) ore type C was agglomerated with 2.2 kg H₂SO₄/t ore and cured for 24 hours before being placed into the 6 inch (12.5 cm) diameter column.

Solution (raffinate with 30 g/L H₂SO₄ and 5 g/L Fe²⁺) was pumped upflow at a rate of 374 L/h/m₂. The solution was recirculated during 8 days, with the pH maintained at 1.5. The results of the test are presented in Figure 14.

Copper and cobalt extractions had not reached a plateau after 8 days; extractions after 8 days were 90.4% and 87.4% for copper and cobalt, respectively. This result was achieved without using SO₂ during the leach (which would have been problematic in a vat). The resulting leach solution (18 g/L Cu, 2.7 g/L Co, 4.7 g/L Fe, 0.33 g/L Mn) should be easily handled in a conventional Cu solvent extraction circuit. Subsequently, the ferrous sulphate from the copper raffinate could be regenerated using SO₂ in a closed vessel and recycling the ferrous sulphate to another vat.

PILOT PLANT CONFIRMATION ON ORE TYPE C

The use of ferrous sulphate as a reductant for the extraction of cobaltic ores has been confirmed during a pilot plant campaign conducted in 1998 at Lakefield. During that pilot plant trial, 20 tonnes of ore type C were ground to a P₈₀ of ~80 microns and were processed at a throughput of ~60 kg/h using a flowsheet presented in simplified form in Figure 15. The pilot plant was designed based on the laboratory results, partly presented above.

At steady-state, the pilot plant produced leach extractions of 98.1% and 91.8% for copper and cobalt, respectively. The same process could be applied to the heap or vat leaching cobaltic ores, because the generation of the reductant is performed very efficiently outside of the heap or vat, thereby insuring that gaseous emissions of SO₂ are fully controlled.

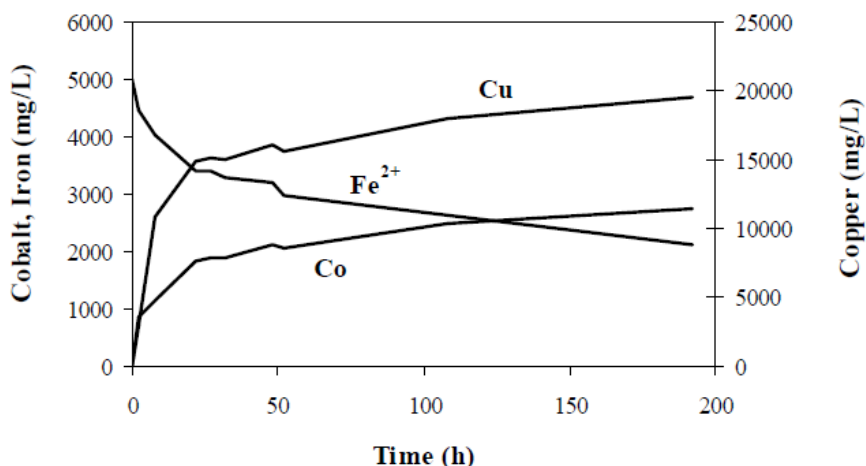


Figure 14 – Vat leaching of ore type C at an initial 5 g/L Fe²⁺ concentration

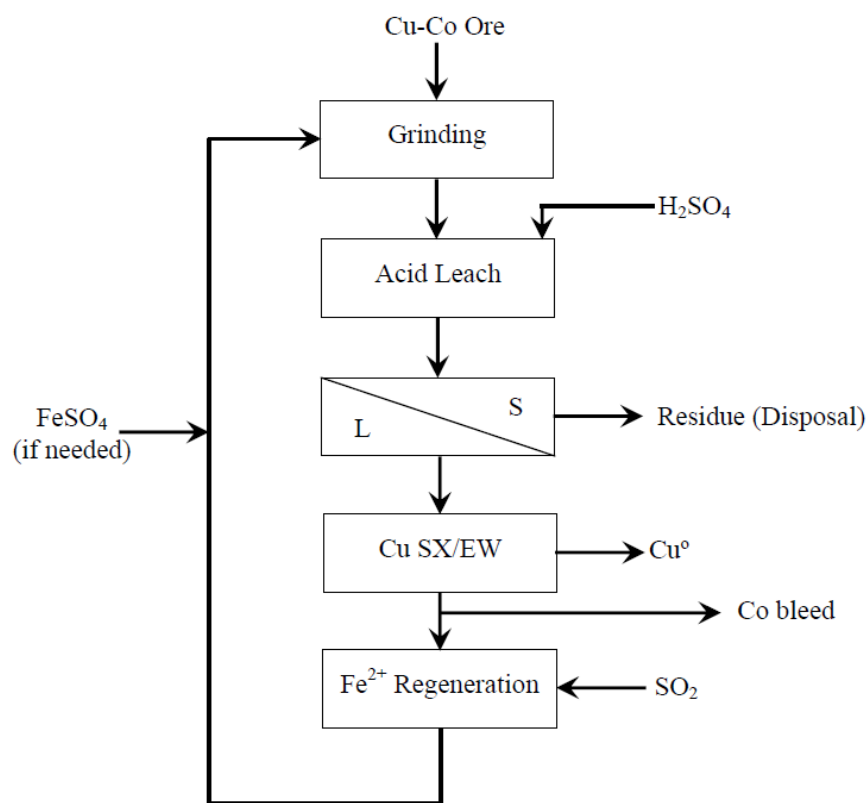


Figure 15 – Pilot plant treatment of ore type C in 1998

CONCLUSIONS

The ferrous/ferric couple has been shown to be of great use in two distinct cases. In the first, iron is used as an oxidant to dissolve secondary copper sulphides and zinc sulphides. Ferric can be regenerated using oxygen, or even faster using SO₂/O₂ mixtures. The question raised when using the Fe²⁺/Fe³⁺ couple to leach metal sulphides is how to separate the metal of value (here copper or zinc) from the iron, so

that good quality metal can be produced and/or the iron recycled. In the case of copper sulphides, the separation of the copper from the iron is not an issue because of the availability of commercial solvent extractants, even though ferric ion is somewhat extracted at the higher pH values. In the case of zinc, that issue still remains, although the solution appears nearer than it was a few years ago. A large scale commercial operation has been operating in Namibia for several years that uses solvent extraction to produce SHG zinc. The extractant used

is DEHPA; DEHPA extracts ferric ions strongly, but not ferrous. There is a good possibility that it could be used to separate the iron from the zinc as long as the iron is kept in the ferrous state, and possibly with a regeneration step to strip any ferric iron that has been extracted by DEHPA. The possibility of extracting iron selectively from the zinc has also been demonstrated at the laboratory scale. Finally, the zinc-iron solution could be blended with the leach solution from an existing RLE plant (if there is one), thereby sacrificing the iron.

The use of SO_2/O_2 mixtures together with the $\text{Fe}^{2+}/\text{Fe}^{3+}$ couple for leaching metal sulphides has to be considered with respect to the sulphate balance in the overall circuit. Its use will have to be examined in detail, case by case, and will depend in particular on the acid consumption of each particular concentrate. In the second case examined, the $\text{Fe}^{2+}/\text{Fe}^{3+}$ couple was used to leach cobaltic oxide ores. The results were very promising concerning the efficiency of the process and the regeneration of the reductant; the process was moreover demonstrated in a relatively large scale pilot plant. Here too, the remaining issue would be to develop an efficient means to separate the iron from the cobalt in the cobalt bleed, and, in this particular case, oxidation-precipitation of the iron should be effective and selective towards cobalt.

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