BASIC IRON SULPHATE – A POTENTIAL KILLER FOR PRESSURE OXIDATION PROCESSING OF REFRACTORY GOLD CONCENTRATES IF NOT HANDLED APPROPRIATELY

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ABSTRACT

Refractory gold concentrates often contain sub-microscopic gold that is encapsulated within the crystal matrix of iron sulphide minerals such as pyrite, pyrrhotite and arsenopyrite. To recover the gold, the host mineral must generally be broken down chemically, by oxidative processes such as roasting, pressure oxidation or bacterial leaching, which expose the gold for subsequent recovery by leaching in cyanide solution. The focus of attention in these pre-treatment processes is usually the oxidation of the sulphides to elemental sulphur, sulphur dioxide gas or sulphate ions. Less attention is paid to the deportment of iron and the changes in its oxidation state, although this can have a profound effect on gold and silver liberation, as well as down stream operating costs.

Iron sulphide minerals break down completely during pressure oxidation, and dissolve in the sulphuric acid solution that is generated from oxidation of the sulphides. This liberates the tiny gold particles that were originally trapped in the sulphide crystals, and gold recovery during subsequent cyanidation is usually very high (>95%). Iron goes into solution in the oxidation process, initially as ferrous sulphate, but this is rapidly oxidized to ferric sulphate, which then hydrolyzes and re-precipitates. The form of the precipitate varies depending on the operating conditions in the autoclave and the presence of certain metal cations. When the acidity in the autoclave is quite low (<20 g/L H_2SO_4) and the temperature is high (>200^{O}C) the formation of hematite is favoured. When the acidity is high (>20 g/L H_2SO_4) and the temperature is relatively low (160 to 200^{O}C), the formation of basic iron sulphate is favoured. If the ore or the leach solution contain significant levels of certain cations (such as Na^+, K^+, NH_4^+, Ag^+ or Pb_2^+) and the acidity is high (>20 g/L H_2SO_4), jarosite compounds are favoured.

Hematite is the desired iron product in the autoclave discharge, for both metallurgical and environmental reasons, but it is difficult to operate an autoclave under the conditions required for effective liberation of gold without converting some of the iron to basic iron sulphate and/or jarosite. These compounds fall into a category of iron compounds known generically as iron hydroxy sulphates, all of which can cause significant processing and environmental problems in the downstream gold process.

This paper deals specifically with basic iron sulphate; the conditions under which it is formed in an autoclave, the problems that are caused by its presence in the feed to a cyanidation plant, and possible remedial strategies that can be adopted, both in the autoclave and downstream.

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INTRODUCTION

It is a fact of life in the gold industry today that most significant new gold discoveries are in sulphide ore bodies that yield poor to modest gold recovery by the traditional whole ore cyanide leaching process. The gold in these deposits is inevitably encapsulated as sub-micron sized particles within an impervious sulphide mineral matrix, and is termed refractory. The most common refractory gold sulphide hosts are arsenopyrite and pyrite, and in order to achieve acceptable gold recoveries, it is generally necessary to break down the host mineral chemically.

This is done by roasting, bacterial oxidation or pressure oxidation processes, in which the sulphide component of the host mineral is oxidized with oxygen to elemental sulphur, sulphur dioxide gas or sulphate ions. There are a great many operating plants around the world employing one or other of these 3 processes to oxidize sulphides ahead of a traditional gold recovery process.

Roasting was the method of choice up to 20 years ago, and is still favoured in some parts of the world. Although it has some advantages over the two hydrometallurgical processes, it has fallen from favour in recent years, mainly because of stringent environmental regulations relating to gas phase emissions, particularly arsenic oxide, but also sulphur dioxide. Bacterial oxidation was seen by some as a saviour for the industry in the 1980's, and a number of small plants were built in Australia and South Africa. But this process has not developed at the rate that was predicted, and there are still technical and infrastructural hurdles that need to be surmounted before this process becomes a catchall for refractory gold ores. There are less than 10 plants in operation world wide today using this technology.

Pressure oxidation technology was developed more than 50 years ago for the treatment of base metal concentrates (mainly sphalerite), and was adapted in the 1980's for the treatment of gold-containing pyrite and arsenopyrite ores and concentrates. The conditions that have evolved for oxidation of refractory gold concentrates are somewhat harsher (T > 190^{O}C) than those used in the base metal operations (T = 150 -170^{O}C) because of the need to oxidize the sulphides all the way through to sulphate, rather than producing elemental sulphur. The latter is favoured in base metal operations owing to the ~ 3 times lower oxygen consumption required for sulphur formation versus sulphate, and the resulting significant reduction in operating costs. But sulphur is an undesirable product in the feed to a gold cyanidation plant, as it reacts with cyanide to form thiocyanate ions. This results in very high cyanide consumption as well as other operating and environmental problems associated with high levels of thiocyanate.

Typical autoclave operating conditions for a refractory gold process are a temperature of 190 to 230^{O}C, and an oxygen over-pressure of 350 to 700 kPa (50 to 100 psi). The oxidation of sulphides are strongly exothermic reactions, and the pulp density of the feed to the autoclave is calculated based on the sulphide concentration in such a way as to provide sufficient heat from the oxidation reaction to maintain the operating temperature of the autoclave at the desired level.

The ideal pulp density for a pyrite-containing feed can be calculated from the following formula, developed by Conway and Gale [1]

Pulp Density = 100/{0.3[S^{2-}] + 0.825}

This formula is often used as a guide for designing the optimum plant operating conditions, although in practice it is prudent to design for the provision of supplemental heating or cooling. All sulphide minerals are oxidized quite rapidly under these conditions, and a residence time of the slurry in the autoclave of 1 to 2 hours is typical.

PROCESS CHEMISTRY

The following oxidation and hydrolysis reactions occur in the autoclave when oxygen is the oxidant and pyrite and arsenopyrite are the dominant sulphide minerals (which is a typical situation with refractory gold projects):

OXIDATION REACTIONS

$2FeS_2 + 7O_2 + 2H_2O = 2FeSO_4 + 2H_2SO_4$	(1)
$4FeSO_4 + 2H_2SO_4 + O_2 = 2Fe_2(SO_4)_3 + 2H_2O$	(2)
$4FeS_2 + 15O_2 + 2H_2O = 2Fe_2(SO_4)_3 + 2H_2SO_4$	(1) + (2) = (3)
$4FeAsS + 11O_2 + 2H_2O = 4HAsO_2 + 4FeSO_4$	(4)
$HAsO_2 + 2FeSO_4 + H2SO_4 + O_2 = Fe_2(SO_4)_3 + H_3AsO_4$	(5)
$4FeAsS + 13O_2 + 2H_2SO_4 + 2H_2O = 2Fe_2(SO_4)_3 + 2H_3AsO_4 + 2HAsO_2$	(4) + (5) = (6)

HYDROLYSIS REACTIONS

$Fe_2(SO_4)_3 + 3H_2O = Fe_2O_3 + 3H_2S\ O_4$ (hematite)	(7)
$4FeS_2 + 15O_2 + 8H_2O = 2Fe_2O_3 + 8H_2SO_4$ (oxidation + hydrolysis)	(3) + (7) = (8)
$Fe_2(SO_4)_3 + 2H_2O = Fe(OH)SO_4 + H2SO_4$ (basic iron sulphate)	(9)
$3Fe_2(SO_4)_3 + 14H_2O = 2H_3OFe_3(SO_4)_2(OH)_6$ (hydronium jarosite)	(10)
$3Fe_2(SO_4)_3 + M_2SO_4 + 12H_2O = 2MFe_3(SO_4)_2(OH)_6 + 6H_2SO_4$ (M = Ag+, NH_4^+, K^+, $1/2Pb^{2+}$)	(11)
$Fe2(SO_4)_3 + 2H_3AsO_4 = 2FeAsO_4 + 3H_2SO_4$ (ferric arsenate)	(12)
$2FeAsS + 7O_2 + 2H_2O = 2FeAsO_4 + 2H_2SO_4$ (oxidation + hydrolysis)	(6) + (12) = (13)

The iron in both pyrite and arsenopyrite is initially oxidized to the ferrous state (equations 1 and 4), and the ferrous is then oxidized more slowly to the ferric state (equations 2 and 5). Most of the ferrous is oxidized to ferric (Fe^{3+}/Fe^{2+} > 10) in the typical 1 to 2 hours residence time in the autoclave, and the emf potential of the autoclave discharge solution should ideally be >500 mV (versus the Ag/AgCl electrode). The overall oxidation reaction generates sulphuric acid in the case of pyrite (equation 3), but consumes acid in the case of arsenopyrite (equation 6). However, when oxidation and hydrolysis are taken into consideration, both minerals are sulphuric acid generators (equations 8 and 13) The sulphide ion in pyrite and arsenopyrite is oxidized all the way to sulphate under aggressive autoclave operating conditions, consuming 3.50 to 3.75 moles of oxygen per mole of pyrite or arsenopyrite in the concentrate (equations 3 and 6). Sulphate is present in both the solution phase (as sulphuric acid and ferric sulphate) and the solid phase (as jarosite or basic iron sulphate), and is distributed 50 to 80% as sulphuric acid, 10 to 30% as ferric sulphate and 0 to 40% as basic iron sulphate or jarosite. As discussed in more detail below, this distribution is influenced quite significantly by the operating conditions in the autoclave and immediately after discharge.

The complete breakdown and dissolution of pyrite and arsenopyrite is highly desirable from a gold recovery perspective, since the fine particles of gold that were trapped within the crystal lattice of the non-porous sulphide particles are completely liberated. This is in contrast to the roasting process, where the iron in pyrite and arsenopyrite is converted to hematite in an all solidstate reaction. The original crystal structure of the sulphide minerals is transformed during roasting, but there is always the possibility that gold particles trapped in the sulphide particles will remain trapped in the hematite particle. Because of this, gold recovery after oxidation of sulphides in an autoclave is typically 5 to 10% better than after oxidation in a roaster.

The extent and distribution of the hydrolysis/precipitation reactions shown in Equations 7, 9, 10, 11 and 12 depend on the temperature and residence time in the autoclave, as well as the acidity of the solution and the concentration of cations such as Na^+, K^+, NH_4^+ and Pb^{2+}. The formation of hematite in equation 7 and ferric arsenate in equation 11 are highly desired reactions, and are favoured at lower free acid concentrations and higher temperatures in the autoclave. Both are very stable compounds, and their presence in tailings is desirable from an environmental perspective. In particular, ferric arsenate is recognized by environmental authorities and regulators as an acceptable form of arsenic for safe disposal to tailings ponds. In addition, both hematite and ferric arsenate form porous precipitates that do not interfere with the subsequent gold recovery process and both are relatively easy to handle as far as their settling, thickening and filtration characteristics are concerned.

The formation of jarosites and basic iron sulphate occurs at higher free acidities in the autoclave (equations 9, 10 and 11). These products are far less desirable because they cause both environmental and processing problems. For example, silver jarosite is a very stable, insoluble compound, which inevitably forms when sulphide concentrates containing appreciable amounts of silver are oxidized in an autoclave. Silver cannot be recovered from silver jarosite by normal cyanidation, and the jarosite has to be decomposed to liberate silver. The established method involves treating the autoclave residue with a strongly alkaline lime solution at high atmospheric temperature (the so-called "lime boil" process). This process is costly and generally unjustifiable except when the silver concentration and/or price are very high. In addition, jarosites create environmental problems in tailings ponds, as they break down slowly over many years, releasing acid and heavy metals to the environment.

Basic iron sulphate is even less stable than jarosite, and this causes worse processing problems in the subsequent cyanidation process for gold/silver recovery; problems that impact both the economics of the process as well health and safety. The economic problems presented by basic iron sulphate relate to the fact that the compound is stable under acidic conditions (from pH 1 to 7), but breaks down at higher pH. This means that the acid that is tied up with basic iron sulphate cannot be neutralized with inexpensive limestone, but reacts readily with expensive lime. The compound consumes about 8 kg/t lime for every 1% sulphate in the autoclave residue, according to the following equation:

$$Fe(OH)SO_4 + Ca(OH)_2 = Fe(OH)_3 + CaSO_4 \quad (14)$$

It is not uncommon to generate autoclave residues containing 10 to 20% sulphate, and this amount of sulphate will consume 75 to 150 kg/t of lime. In addition, the large amounts of fine ferric hydroxide and gypsum precipitate that are generated can drastically alter the rheological properties of the slurry feeding the cyanidation plant, creating pumping, mixing, settling and oxygen mass- transfer problems.

The health and safety issue relates to the fact that basic iron sulphate reacts very slowly with lime at room temperature, and complete neutralization of all the acid can take 12 to 24 hours. During this time, the pH increases rapidly to the desired range of 10 to 11 when lime is added, but then drifts slowly down to the pH 7 to 9 range over the next half hour or so. If cyanide is added before all the acid has been neutralized, there is a risk that free cyanide will be converted to HCN gas when the pH drops below ~9.5, exposing workers to a potentially hazardous situation. Therefore, it is important to neutralize all the acid before adding cyanide, and this takes a long time, increasing tankage requirements, plant foot print and capital cost.

Although formation of the desired hematite and ferric arsenate hydrolysis products is favoured at low acidities (< 20 g/L H_2SO_4) and high temperatures (> 200^{O}C), in practice it is costly to operate an autoclave under conditions in which these are the dominant iron hydrolysis products in the solid phase. For example,

operating at higher temperatures increases plant capital costs because of the increased pressure rating needed for the autoclave vessel and the feed pumps. Moreover, in order to generate a low acid concentration in solution in the autoclave, it is necessary to feed the autoclave at a low pulp density, and this in turn increases the size of the autoclave (increasing capital costs) for a given concentrate feed rate and residence time. In addition, if the pulp density is below the optimum value required for autothermal operation, heat has to be recovered from the discharge and used to pre-heat the feed, which also increase capital cost. Because of these significant capital cost considerations, commercial autoclaves are generally operated under conditions in which the formation of basic iron sulphate is a reality.

THE "HOT CURE PROCESS" – THE SOLUTION TO THE BASIC IRON SULPHATE PROBLEM

The solution to the problems posed by basic iron sulphate formation is a simple one, and derives from the fact that the hydrolysis reaction that results in the formation of basic iron sulphate at high temperatures in the autoclave is reversible at lower temperatures. A diagram showing areas of stability of various compounds in the Fe-S-O system as a function of temperatu re and pH is presented in Figure 1, with the area of stability of jarosite highlighted.

Although the area of stability for basic iron sulphate was not reported in the original publication [2], it is assumed to be similar to jarosite, except diminished in size somewhat because of its lower stability than jarosite. It can be seen from Figure 1 that jarosite and basic iron sulphate will form under acidic conditions (pH <2) and at high temperatures (>140^{O}C). It should also be apparent from Figure 1 that jarosite and basic iron sulphate will break down under more strongly acidic conditions (pH < 1) and at lower temperatures (<140^{O}C), and this is the basis of the "Hot Cure" process [3]. This acidic reaction consumes acid and produces ferric sulphate in solution, and is the reverse of reactions (9) and (11) for the formation of basic iron sulphate and jarosite:

$$2Fe(OH)SO_4 + H_2SO_4 = Fe_2(SO_4)_3 + 2H_2O \quad (15)$$

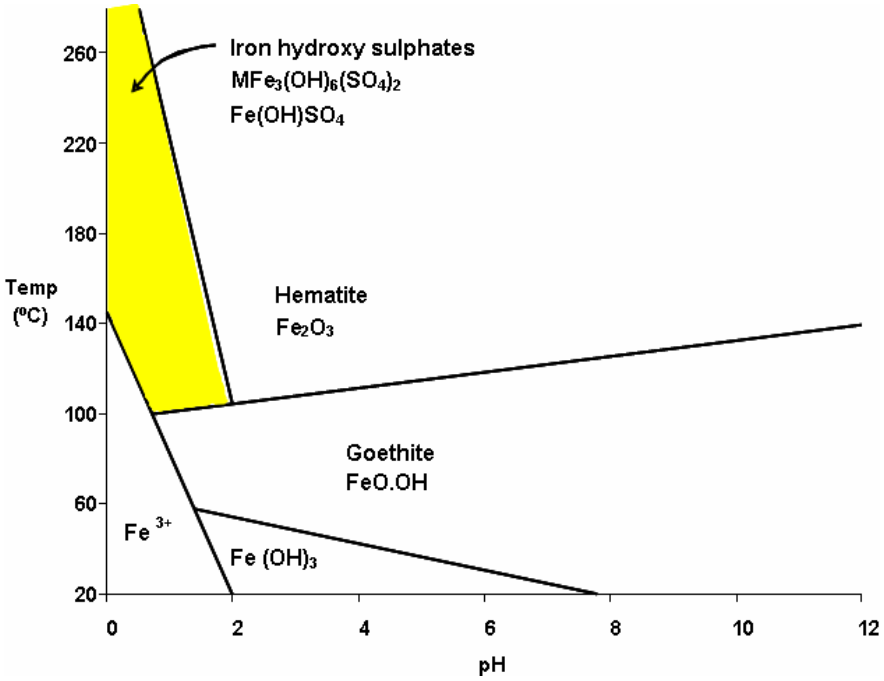

Figure 1 Areas of stability of various compounds in the Fe-S-O system (After Babcan [2])

It should also be clear from Figure 1 that basic iron sulphate and jarosite will break down under alkaline conditions (pH >2) to form either hematite (at temperatures > 100^{O}C), or goethite (at moderate temperatures of 60 to 100^{O}C). This is the basis of the Lime Boil process developed by Sherritt [4], to liberate silver from the stable silver jarosite complex. In practice, strongly alkaline conditions and high temperatures are required to drive these reactions to completion, and large amounts of expensive lime are consumed. This is the main draw back of the Lime Boil process.

The Hot Cure process, on the other hand, uses acid and heat that have already been generated in the autoclave, to break down the basic iron sulphate, so requires no additional reagent and minor additional energy cost.

After the Hot Cure process is complete, the residual sulphuric acid as well as the ferric sulphate generated during hot curing can be neutralized with limestone:

$$Fe_2(SO_4)_3 + 3CaCO_3 + 3H_2O = 2Fe(OH)_3 + 3CaSO_4 + 3CO_2 \quad (16)$$

Therefore, the main advantage of the Hot Cure process is that it allows the ferric sulphate and acid generated in the autoclave to be neutralized with limestone, rather than lime. Depending on the region of the world that the autoclave is operating and the local availability of limestone, its cost could be up to 10 times lower than that of hydrated lime.

An added advantage of the Hot Cure process is that it allows the ferric sulphate and acid in the Hot Cure liquor to be separated from the autoclave discharge solids (by filtration or countercurrent decantation) prior to neutralization. This in turn allows the ferric hydroxide and gypsum precipitates to be kept out of the pulp phase feeding the cyanidation process, which mitigates their potential negative impact on rheology and mass-transfer during gold leaching.

The gypsum and ferric hydroxide products of equation 15 would normally be sent to a thickener, with the thickener underflow joining the tailings from the gold recovery operations for discharge to a common tailings facility, and the thickener overflow either being recycled to the plant as process water or treated for base metal recovery.

A simplified flowsheet for a refractory sulphide pressure oxidation/cyanidation process incorporating hot curing is shown in Figure 2. The hot autoclave discharge would normally be pumped directly to the hot curing tank, without any intermediate thickening, solid liquid separation or cooling stages. The slurry would then be held in the 90 to 100°C temperature range for 2 to 12 hours, using supplemental steam from the autoclave to maintain the temperature.

Laboratory and pilot plant test data will be drawn from three recent projects conducted at SGS Minerals' Lakefield facility (Quimsacocha, Pueblo Viejo and Gold Fields' Driefontein tailings treatment project in South Africa), to illustrate the potential impact of basic iron sulphate formation, and the benefits of the Hot Cure Process [3].

THE QUIMSACOCHA PROJECT

The Quimsacocha project in Ecuador is owned by Iamgold Corporation. Gold is locked in a sulphide matrix comprising mainly pyrite and enargite, and the flowsheet that is currently favoured (at the pre-feasibility stage) on technical and environmental grounds, involves flotation to produce a bulk sulphide concentrate, followed by pressure oxidation of the concentrate. Copper reports to the autoclave liquor, from where it will probably be recovered by conventional solvent extraction and electrowinning, while gold and silver will be recovered from the autoclave solids by conventional cyanidation and either Merrill Crowe cementation or adsorption on activated carbon.

This flowsheet is favoured because:

- Arsenic is stabilized in the solid phase tailings as scorodite, $FeAsO_4$
- Copper is readily recovered as a high value product
- Gold and silver are recovered very efficiently (>90%)

Initial autoclave test work showed that most of the iron in the autoclave feed was converted to basic iron sulphate under the preferred autoclave operating conditions, and that the solid residue (after filtration and washing) consumed vast amounts of lime during neutralization. The results of two batch

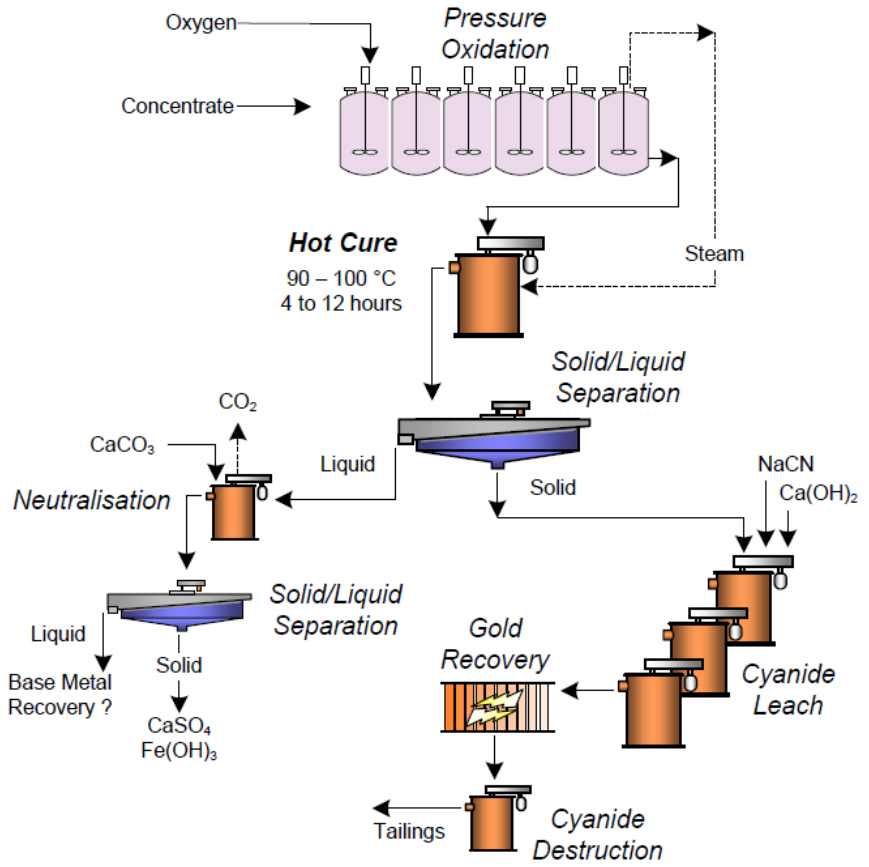

Figure 2 Refractory gold pressure oxidation, hot curing and cyanidation flowsheet Results

autoclave tests that were carried out with a bulk rougher flotation concentrate from the Quimsacocha project are presented in Table 1. In one test the hot autoclave discharge slurry was filtered and the solids were thoroughly washed with water prior to cyanidation. In the other, the autoclave discharge was maintained for several hours at 90°C (i.e. hot cured), prior to filtration and washing. Both autoclave tests were carried out under optimum autoclave conditions that had been established previously (20% solids density, 200°C temperature, 100 psi oxygen partial pressure, 2 hour residence time).

Table 1 Results from batch autoclave autoclaving of rougher concentrates from the Quimsacocha project in Ecuador

SPECIES	FEED CONC	TST 1 AUTOCLAVE ONLY		TEST 2 AUTOCLAVE + HOT CURE	
	%	Residue	Solution	Residue	Solution
		%	g/L	%	g/L
Cu	1.38	0.007	1.72	0.007	1.75
As	0.47	0.33	0.13	0.1	0.55
Fe	24	13.6	10.2	3.6	26.2
S^{2-}	26.4	<0.05	na	<0.05	na
$[S]_{total}$	27.8	6.38	na	1.2	na
$[SO_4]_{total}$	0	20	72	2.9	100
H_2SO_4	0	0	43	0	30

The sulphate to iron ratio in the solid residue from the first test (autoclave only) shows that the iron was converted from pyrite and enargite in the autoclave feed to predominantly basic iron sulphate in the residue. The theoretical mass ratio of sulphate to iron in basic iron sulphate (96/56) is 1.7, which means the sulphate content of the first test residue (20%) would have tied up 11.8% of the iron in the residue if it was there as basic iron sulphate. Since the total iron in the residue was only 13.6%, the

results suggest that almost 90% of the iron was converted to basic iron sulphate under the optimum operating condition, and less than 15% to hematite.

After hot curing, the sulphate content of the solids had decreased to 2.9% and iron to 3.6%, and almost 90% of the original basic iron sulphate content of the residue had decomposed. It can be calculated that about half the iron in the Hot Cure residue was present as hematite and half as basic iron sulphate. This portion could presumably have been reduced to zero under more aggressive hot curing conditions.

The rate of decomposition of the basic iron sulphate in the Quimsacocha autoclave residue is illustrated in Figures 3 and 4. The data in Fig. 3 show the changing concentrations of Fe and SO_4 in the solids as a function of time, and the mass ratio of the change (ΔSO_4/ΔFe) is very close to the theoretical ratio of 1.7 that would be expected for basic iron sulphate. This confirms the 1:1 molar ratio for the formulation of basic iron sulphate {$Fe(OH)SO_4$} rather than a formulation such as that of hydronium jarosite {$HFe_3(OH)_6(SO_4)_2$}, which needs a Fe to SO_4 molar ratio of 1.5.

The data in Fig. 4 show the rate of change of the solution composition during hot curing, which confirms that the process leads to an increase in the concentration of ferric ion in solution and a decrease in the concentration of sulphuric acid, as would be expected from Equation 14. It should be noted that chemical analysis indicated that >99% of the iron in solution was in the ferric form after both autoclaving and hot curing, which confirms that the iron in the basic iron sulphate complex is in the ferric form.

Limestone consumption by the autoclave liquor and the wash water almost doubled after hot curing, from 370 kg per ton of concentrate in the autoclave discharge liquor to 704 kg/t in the Hot Cure discharge liquor, because of the higher concentration of ferric sulphate in the latter solution (Equation 16). However, as shown below, this increase was compensated by a more than 10-fold decrease in lime consumed during cyanidation, which is considerably more expensive than limestone.

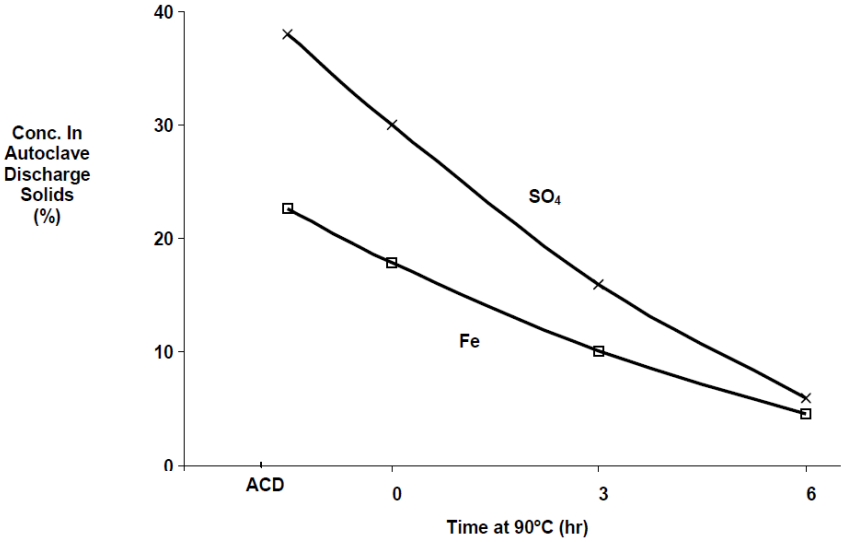

Figure 3 Concentrations of iron and sulphate in the solid residue discharge from autoclaving Quimsacocha flotation concentrate as a function of hot curing time

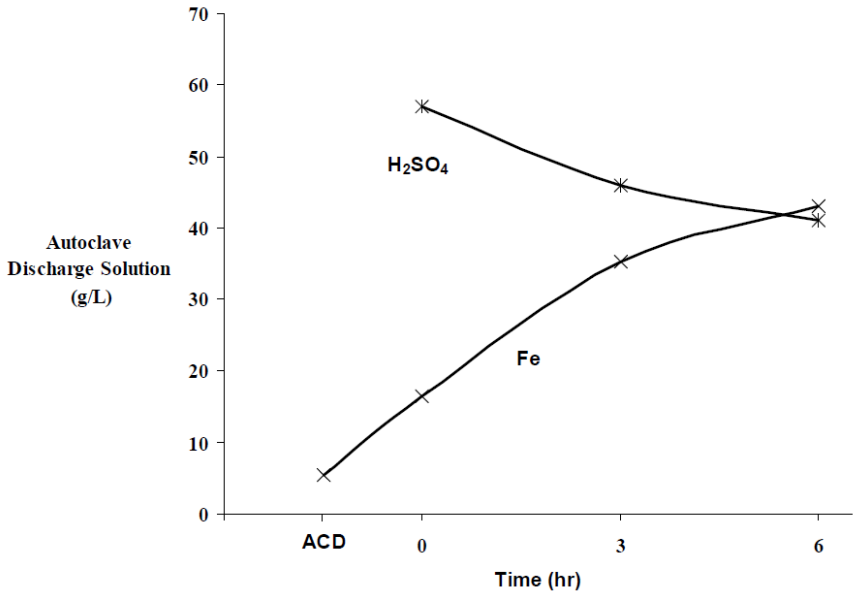

Figure 4 Concentrations of iron and sulphuric acid in solution in the discharge from autoclaving Quimsacocha flotation concentrate, as a function of hot curing time.

The washed solid residues from the two autoclave tests were subjected to cyanidation and carbon in leach (CIL), to dissolve the gold and silver and load it onto activated carbon. The results of these two tests are summarized in Table 2.

Table 2 Results from batch cyanidation and CIL treatment of Quimsacocha rougher flotation concentrates after oxidation of the sulphides by autoclaving.

	UNITS	AUTOCLACVE RESIDUE	AUTOCLAVE + HOT CURE RESIDUE
Au feed grade	g/t	23.7	23.7
Au CN residue	g/t	0.08	0.17
Au extracted	%	99.6	99.4
Ag feed grade	g/t	97	97
Ag CN residue	g/t	3.8	10
Ag extracted	%	94.8	90
NaCN consumed	kg/t	1.75	2.92
Lime consumed	Kg/t	213	18.9

Gold recovery was very similar in both tests, but silver recovery was slightly lower after hot curing. A loss in silver recovery during hot curing is not uncommon, and is thought to be due to the slow formation of silver jarosite during hot curing. In the Quimsacocha case, savings in lime consumption will more than compensate for slight losses in silver recovery, and installation of the Hot Cure process will result in a significant lowering of operating costs for minimal capital investment.

THE PUEBLO VIEJO PROJECT

The second example is drawn from the Pueblo Viejo project in the Dominican Republic. The pilot plant test work was carried out in Lakefield in the early 2000's for the previous owners of Pueblo Viejo, Placer Dome Corporation of Canada. The theory and practice of the hot cure process was developed during this project, and is the subject of a patent application [3]. When Placer Dome was acquired by Barrick Gold, they continued to evaluate the project and made the decision in 2005 to proceed with a commercial installation. The Pueblo Viejo flowsheet involves whole ore pressure oxidation, followed by CCD to separate the autoclave liquor from the oxidized solids, which are then processed by cyanidation and CIL to recover gold and silver.

Considerably less basic iron sulphate was formed when Pueblo Viejo ore was pressure oxidized under optimum conditions (225^{o}C, 100 psi oxygen, 60 minutes residence time) than in the Quimsacocha project, because of the lower concentration of sulphide in the whole ore Pueblo Viejo autoclave feed (~4%) than the Quimsacocha concentrate autoclave feed (~20%). But even in this case, based on the sulphate (~11%) and Fe (~6%) contents of the autoclave residue, it is apparent that almost all of the iron in the Pueblo Viejo ore was converted to basic iron sulphate under the optimum autoclave operating conditions, and very little to hematite .

The rate of decomposition of basic iron sulphate during hot curing of the pressure oxidized Pueblo Viejo ore at 90^{o}C is shown in Figures 5 and 6. As predicted from Equation 15, Fe and SO_4 in the solids decreased with time, as did sulphuric acid in solution, while Fe in solution increased.

To determine the economic impact of hot curing in this operation, both the autoclave and the Hot Cure residues were filtered, washed and treated by cyanidation and CIL. Average results from these tests are presented in Table 3.

Gold recovery was very similar in both cases, but silver recovery deteriorated from about 80% to less than 10% after hot curing. Although lime consumption was significantly lower in the hot cured residue than the autoclave residue

Table 3 Results from batch cyanidation and CIL treatment of Pueblo Viejo ore after oxidation of the sulphides by autoclaving

PRODUCT	RECOVERY		ALKALI CONSUMED		APPROX ALKALI COST
	Au%	Ag%	$CaCO_3$ kg/t	$Ca(OH)_2$ g/t	$/t
Autoclave Discharge	96.7	78.5	110	62	10.5
Hot Cure Discharge	96.3	3.5	195	8	3.2

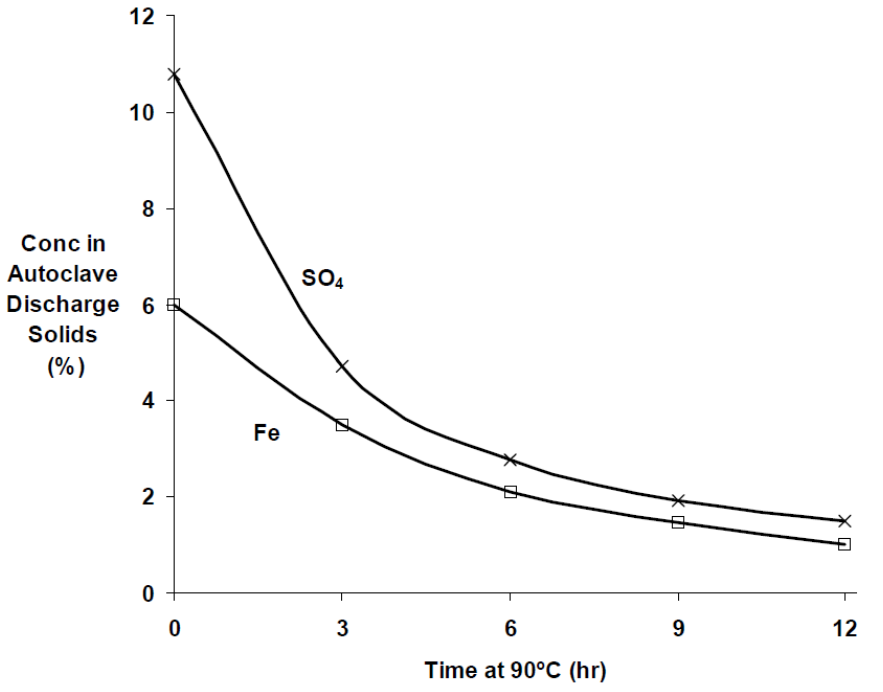

Figure 5 Concentrations of iron and sulphate in the solid residue from autoclaving Pueblo Viejo ore, as a function of hot curing time.

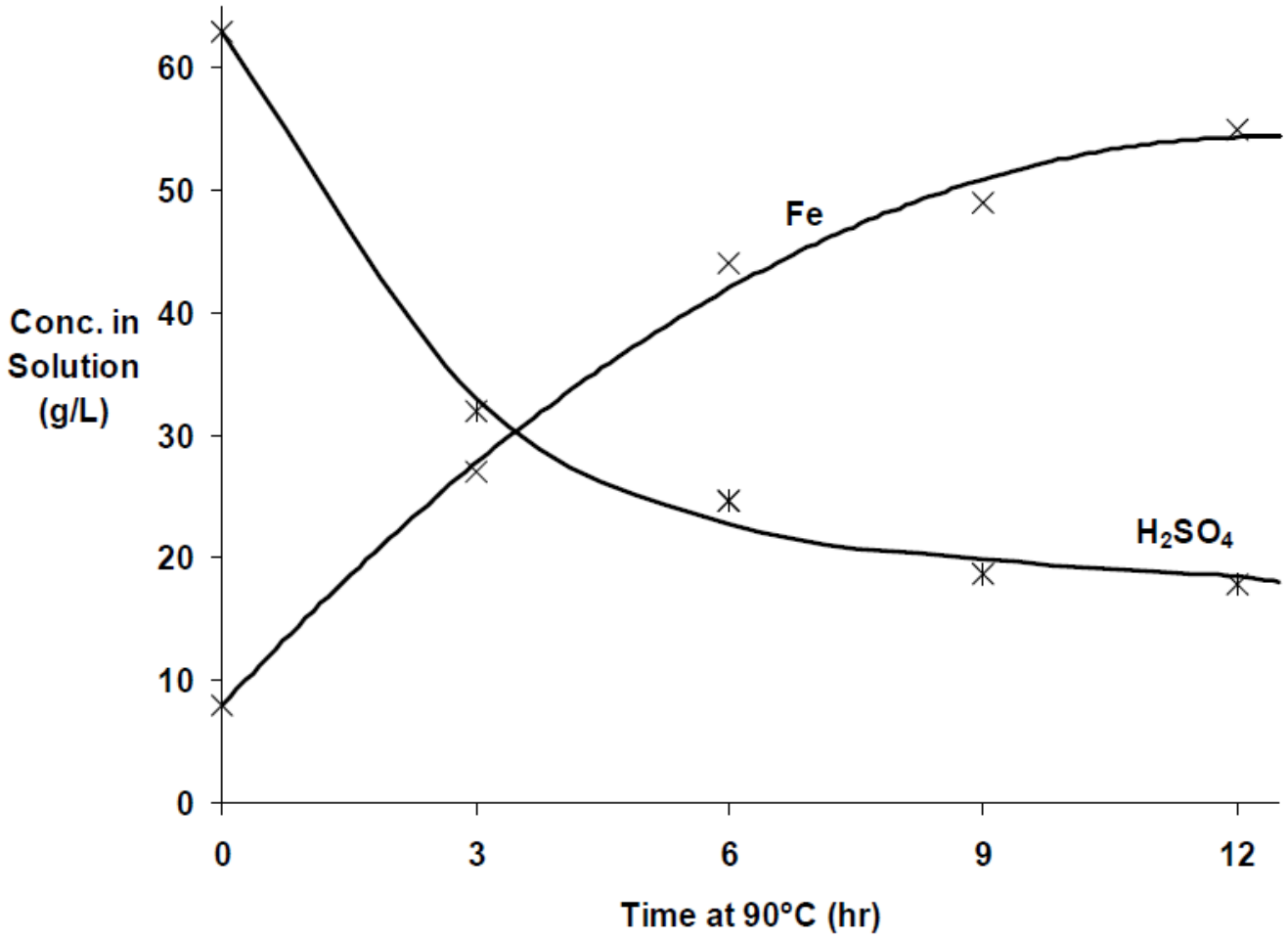

Figure 6 Concentrations of iron and sulphuric acid in solution in the discharge from autoclaving Pueblo Viejo ore, as a function of hot curing time

(decreasing from ~60kg/t to < 10 kg/t), the savings in operating costs due to lower lime consumption would not have compensated the loss of silver recovery (approx half an ounce of silver), and the decision was therefore taken not to incorporate hot curing in the full scale Pueblo Viejo plant, at least until a way of lowering lime consumption without compromising silver recovery is found. One possibility that might be worth investigating in the future would be to operate a hybrid Hot Cure/Lime Boil process. By operating a Hot Cure process before lime boiling, most of the sulphate in the autoclave residue can be decomposed and washed from the solids prior to lime boiling. This should significantly lower lime consumption in the Lime Boil process, which is its main negative feature.

DRIEFONTEIN TAILINGS RE-TREATMENT PROJECT

In a third investigation, which examined the recovery of gold and uranium from Gold Field's gold mine tailings in South Africa, a rougher pyrite concentrate was produced from the tailings, which was then cleaned to produce high grade and low grade components. The high grade component was oxidized in an autoclave and the hot autoclave discharge was then combined with the low grade component in an atmospheric leach.

In this case, one of the objectives of the autoclave process was to produce as much ferric ion as possible, to oxidize the uranium (IV) in the re-combined rougher concentrate to the U(VI) oxidation state, and as much sulphuric acid as possible, to react with acid-consuming gangue in the cleaner tails and solubilize the uranium.

From the above equations, it is apparent that when pyrite or any other iron sulphide mineral is oxidized in an autoclave, the main products will be ferric sulphate and sulphuric acid in solution, and hematite and basic iron sulphate in the solids. The sulphate ion is common to all the products except hematite, which is generally the most desired product.

To determine the influence of autoclave temperature and hot curing on the distribution of sulphate between sulphuric acid, ferric sulphate and basic iron sulphate, three batch autoclave/ Hot Cure tests were performed on the high grade component of the pyrite concentrate, at 190, 210 and 230°C. The effect of temperature on the distribution of iron in the residue between basic iron sulphate and hematite was also examined.

The concentrate contained 17.4% Fe and 15% S^{2-}, and the pressure oxidation tests were conducted at a pulp density of 15% solids. All of the sulphide in the concentrate was fully oxidized (>99%) to sulphate, in all three tests, and this would theoretically have generated 450 kg SO_4 per ton of autoclave feed, based on the 15% S head assay. There was minimal mass loss after autoclaving, but about 20% of the residue mass was lost after hot curing.

Table 4 The effect of autoclave temperature during oxidation of a pyrite concentrate on the concentrations of sulphate and iron products in the autoclave and Hot Cure discharge

TEMP	Concentrations in Solution (g/L)				Concentration in the solids (%)			
°C	H_2SO_4		$Fe_2(SO_4)_3$		SO_4		Fe	
	ACD	HCD	ACD	HCD*	ACD	HCD*	ACD	HCD*
190	49	40	7	11.3	9.9	1.1	16.6	11.4
210	55	46	4.1	7.4	9.4	1.1	18.5	13.6
230	56	50	3.2	6.4	8.4	0.9	19	14.6

ACD = autoclave discharge; HCD = Hot Cure discharge; *Hot Cure discharge concentrations corrected for ~20% mass loss in hot curing

Table 5 The effect of autoclave temperature during oxidation of a pyrite concentrate on the distribution of iron and sulphate iron products in the autoclave discharge

TEMP	Fe distribution in ACD			Sulphate Distribution (kg/t)							
°C	Hem	BFS	FC	H_2SO_4		$Fe_2(SO_4)_3$		$Fe(OH)SO_4$		TOTAL	
			%	ACD	HCD*	ACD	HCD*	ACD	HCD*	ACD	HCD*
190	53	32	15	260	255	102	185	98	11	460	451
210	62	30	8	295	293	43	122	94	11	432	426
230	67	26	7	301	319	34	104	84	9	419	432

Hem=hematite; BFS= basic iron sulphate; FS = ferric sulphate; * Corrected for ~20% mass loss in hot curing

The autoclave solution was analyzed for sulphuric acid and Fe, and the residue was analyzed for Fe and SO_4, both before and after hot curing, and the results are presented in Tables 4 and 5.

The concentrations of acid and iron in the autoclave solution and residue are presented in Table 4, while the distribution of iron between its three autoclave products (hematite, basic iron sulphate and ferric sulphate) and the distribution of sulphate between its three autoclave products (sulphuric acid, ferric sulphate and basic iron sulphate) are shown in Table 5.

The following can be concluded from the results in Tables 4 and 5:

- The amount of sulphate analyzed in the autoclave products ranged from 420 to 460kg/t in the 3 tests, versus the theoretical amount of 450 kg/t, giving an excellent accountability of over 95%.
- The distribution of iron in the autoclave discharge indicated that most was in the form of hematite (50 - 70%), followed by basic iron sulphate (20 to 30%), with only about 10% in solution as ferric sulphate.
- The proportion of hematite increased with increasing temperature, as expected, whilst both basic ferric sulphate and ferric sulphate decreased with temperature. Distributions after hot curing are not shown, but the data suggested that ~90% of the basic iron sulphate decomposed to ferric sulphate during hot curing, and there was no change in the amount of hematite (after correction for mass loss in hot curing).
- Most of the sulphate was converted to sulphuric acid (50 to 70%), and the percentage conversion increased with temperature from ~50% at 190°C to 70% at 230°C. This was followed by ferric sulphate, which accounted for 10 to 20% of the sulphate in the autoclave discharge and 20 to 40% in the Hot Cure discharge. About 15 to 20% of the sulphate was in the form of basic iron sulphate in the autoclave discharge, and >90% of this decomposed to ferric sulphate in solution during hot curing. The proportions of both ferric sulphate in solution and basic iron sulphate in the residue decreased with increasing autoclave temperature.

CONCLUSIONS

Basic iron sulphate is the product of a hydrolysis reaction that occurs when pyrite and other iron sulphide minerals are oxidized to ferric sulphate and sulphuric acid in an autoclave. The proportion of iron in the autoclave feed that is converted to basic iron sulphate increases with increasing ferric ion and sulphuric acid concentrations in solution, and with decreasing temperature in the range 180 to 250°C.

The alternative and much preferred hydrolysis product is hematite, which is favoured at lower acidity in the autoclave solution (10 - 20 g/L) and higher temperatures (> 200°C). In practice, the production of a hematite autoclave residue with minimal basic iron sulphate formation is difficult to achieve without a significant capital cost penalty, and the formation of basic iron sulphate is a reality in all commercial autoclave operations. Whilst this is not much of a problem in base metal pressure oxidation plants, it can cause serious operational, economic, environmental and health and safety problems in downstream cyanidation plants for gold/silver recovery.

Basic iron sulphate is only moderately stable under atmospheric conditions, and can be decomposed either under alkaline conditions, which converts it to ferric hydroxide and gypsum precipitates, or under acidic conditions, which converts it to ferric sulphate in solution. Basic iron sulphate is only truly stable in an autoclave, at high temperatures (> 140°C) and in the presence of reasonably high acid concentrations in solution (> 30 g/L).

If the autoclave discharge is to be leached with cyanide for gold recovery, it is very important to destroy most of the basic iron sulphate in the residue prior to cyanidation. If this is not done, it is very difficult to maintain a pH of > 10, which is needed to maintain cyanide in the free cyanide form rather than

the toxic, gaseous HCN form. The pH constantly drifts downwards due to the slow consumption of lime by basic iron sulphate, which leads to the formation of HCN gas, and creates an unsafe working environment for the gold plant operators. One option is to neutralize the residue with lime at pH >10 prior to cyanidation, to convert the basic iron sulphate to ferric hydroxide and gypsum before the acid and cyanide have a chance to react. But this process is slow (up to 24 hours), consumes vast amounts of lime (up to 200 kg/t is not uncommon) and produces slurry with very poor rheology, owing to the presence of the fine precipitates.

The much preferred option is to break down the basic iron sulphate under acidic conditions in the Hot Cure process [3]. This process is somewhat faster (typically 6 to 12 hours) than high pH neutralization, requires no additional reagents, and most importantly, allows all the iron and acid associated with basic iron sulphate to be neutralized with limestone, at a fraction of the cost of lime. If the solid residue and solution phases are separated by CCD or filtration prior to cyanidation, the precipitates of ferric hydroxide and gypsum that are formed during neutralization with limestone can be kept out of the cyanidation feed, greatly improving slurry rheology in the gold plant (leach and Merrill Crowe, CIP or CIL).

A potential drawback of the Hot Cure process is that silver recovery by cyanidation decreases somewhat after hot curing. This is thought to be due to the slow formation of a silver jarosite compound during hot curing, and the effect can be very minor, as in one case reported here, or it can be very significant, as in another example reported here. In all cases, the operating cost and operational benefits afforded by the Hot Cure process have to be weighed against the loss of revenue due to lower silver recovery.

In those cases where loss of silver revenue is significant to the economics of the project, a possible flowsheet option to investigate would be to operate a hybrid Hot Cure/Lime Boil process. By operating a Hot Cure process before lime boiling, most of the sulphate in the autoclave residue could be decomposed and separated from the solids prior to lime boiling, which should significantly lower lime consumption in the lime boil process.

REFERENCES

Conway, M.H. and Gale, D.C., Sulfurs Impact on the Size of Pressure Oxidation Autoclaves, Journal of Metals, pp 19-22, Sept 1990.

Babcan, J., Synthesis of Jarosite, $KFe_3(SO_4)_2(OH)_6$, Geol Zb., Vol 22(2), pp 299-304, 1971.

Ji, J., King, J.A., Fleming, C.A. and Ferron, C.J., Reduction of lime consumption when treating refractory gold ores or concentrates, U.S. Patent Application No. 11/249,120, Publication No. 2006/0133974 A1, June 2006.

Berezowsky, R.M.G.S and Weir, D.R., Refractory Gold. The Role of Pressure Oxidation. Proceedings of World Gold '89 Symposium, Edited by R.B.Bhappu and R.J Harden. New York. American Institute of Mining Metallurgy and Petroleum Engineers, pp 295 – 304, 1989.

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