

Basic iron sulfate – a potential killer in the processing of refractory gold concentrates by pressure oxidation

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Abstract

Refractory gold concentrates often contain submicroscopic gold that is encapsulated within the crystal matrix of iron sulfide 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 pretreatment processes is usually the oxidation of the sulfides to elemental sulfur, sulfur dioxide gas or sulfate 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 downstream operating costs. Iron sulfide minerals break down completely during pressure oxidation, and dissolve in the sulfuric acid solution that is generated from oxidation of the sulfides. This dissolution liberates the tiny gold particles that were originally trapped in the sulfide crystals, and gold recovery during subsequent cyanidation is usually very high (>95%). Iron goes into solution in the oxidation process, initially as ferrous sulfate, but this compound is rapidly oxidized to ferric sulfate, which then hydrolyzes and reprecipitates. 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 H₂SO₄) and the temperature is high (>200°C), the formation of hematite is favored. When the acidity is high (>20 g/L H₂SO₄) and the temperature is relatively low (160 to 200°C), the formation of basic iron sulfate is favored. If the ore or the leach solution contains significant levels of certain cations (such as Na⁺, K⁺, NH₄⁺, Ag⁺ or Pb²⁺) and the acidity is high (>20 g/L H₂SO₄), jarosite compounds are favored. 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 sulfate and/or jarosite. These compounds fall into a category of iron compounds known generically as iron hydroxy sulfates, all of which can cause significant processing and environmental problems in the downstream gold process. This paper deals specifically with basic iron sulfate: 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.

Key words: Gold/ gold ores, Oxidation processing, Refractory gold processing

Introduction

It is a fact of life in the gold industry today that most significant new gold discoveries are in sulfide 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 submicron-sized particles within an impervious sulfide mineral matrix, and is termed refractory. The most common refractory gold sulfide 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 sulfide component of the host mineral is oxidized with oxygen to elemental sulfur, sulfur

dioxide gas or sulfate ions. There are a great many operating plants around the world employing one or another of these three processes to oxidize sulfides ahead of a traditional gold recovery process.

Roasting was the method of choice up to 20 years ago and is still favored in some parts of the world. Although it has some advantages over the two hydrometallurgical processes, it has fallen from favor in recent years, mainly because of stringent environmental regulations relating to gas phase emissions, particularly arsenic oxide, but also sulfur dioxide. Bacterial oxidation was seen by some as a savior for the industry in the 1980s, 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 worldwide 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 1980s 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 ($T > 190^\circ\text{C}$) than those used in the base metal operations ($T = 150 - 170^\circ\text{C}$), because of the need to oxidize the sulfides all the way through to sulfate, rather than producing elemental sulfur. The latter is favored in base metal operations, owing to the ~3 times lower oxygen consumption required for sulfur versus sulfate formation and the resulting significant reduction in operating costs. But sulfur 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°C, and an oxygen overpressure of 350 to 700 kPa (50 to 100 psi). The oxidation of sulfides are strongly exothermic reactions, and the pulp density of the feed to the autoclave is calculated based on the sulfide 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 (1990).

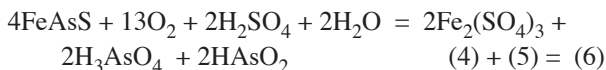
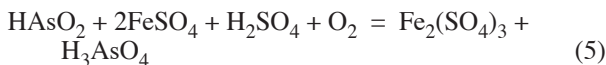
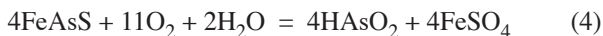
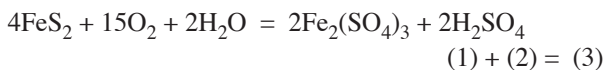
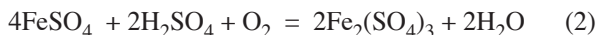
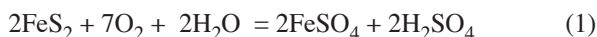
$$\text{Pulp density} = 100 / \{0.3[\text{S}^{2-}] + 0.825\}$$

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 sulfide minerals are oxidized quite rapidly under these conditions, and a residence time of the slurry in the autoclave of one to two hours is typical.

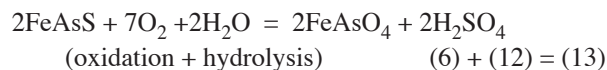
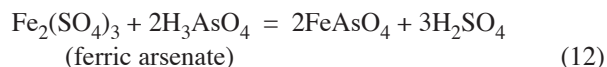
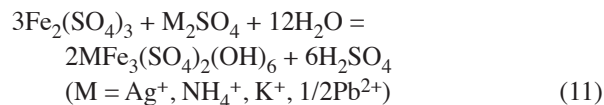
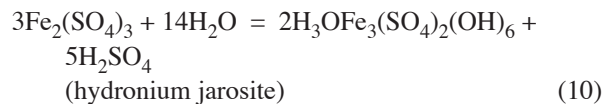
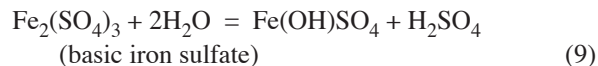
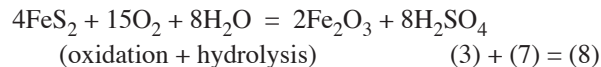
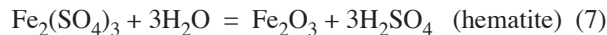
Process chemistry

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

Oxidation reactions (all products are soluble species):



Hydrolysis reactions (all iron products are precipitates):



The iron in both pyrite and arsenopyrite is initially oxidized to the ferrous state, as shown in Eqs. (1) and (4), and the ferrous is then oxidized more slowly to the ferric state, Eqs. (2) and (5). Most of the ferrous is oxidized to ferric ($\text{Fe}^{3+}/\text{Fe}^{2+} > 10$) in the typical one-to-two hours' residence time in the autoclave, and the potential of the autoclave discharge solution should ideally be > 500 mV (versus the Ag/AgCl electrode). The overall oxidation reaction generates sulfuric acid in the case of pyrite, Eq. (3), but consumes acid in the case of arsenopyrite, Eq. (6). However, when oxidation and hydrolysis are taken into consideration, both minerals are sulfuric acid generators (Eqs. (8) and (13)).

The sulfide ion in pyrite and arsenopyrite is oxidized all the way to sulfate under aggressive autoclave operating conditions, consuming 3.50 to 3.75 moles of oxygen per mole of pyrite or arsenopyrite in the concentrate (Eqs. (3) and (6)). Sulfate is present in both the solution phase (as sulfuric acid and ferric sulfate) and the solid phase (as jarosite or basic iron sulfate), and is distributed 50 to 80% as sulfuric acid, 10 to 30% as ferric sulfate and 0 to 40% as basic iron sulfate 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.

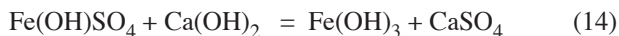
The complete breakdown and dissolution of pyrite and arsenopyrite is highly desirable from a gold recovery perspective, since the fine particles of gold that were trapped within the crystal lattice of the non-porous sulfide particles are completely liberated. This is in contrast to the roasting process, where the iron in pyrite and arsenopyrite is converted to hematite in an all-solid-state reaction. The original crystal structure of the sulfide minerals is transformed during roasting, but there is always the possibility that gold particles trapped in the sulfide particles will remain trapped in the hematite particle. Because of this, gold recovery after oxidation of sulfides 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 Eqs. (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 Eq. (7) and ferric arsenate in Eq. (11) are highly desired reactions, and are favored 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 sulfate occurs at higher free acidities in the autoclave, Eqs. (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 sulfide 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 (Berezowsky and Weir, 1989) 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 sulfate 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 as health and safety. The economic problems presented by basic iron sulfate 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 sulfate cannot be neutralized with inexpensive limestone, but reacts readily with expensive lime. The compound consumes about 8 kg/t lime for every 1% sulfate in the autoclave residue, according to the following equation:



It is not uncommon to generate autoclave residues containing 10 to 20% sulfate, and this amount of sulfate 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 sulfate 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, which takes a long time, increasing

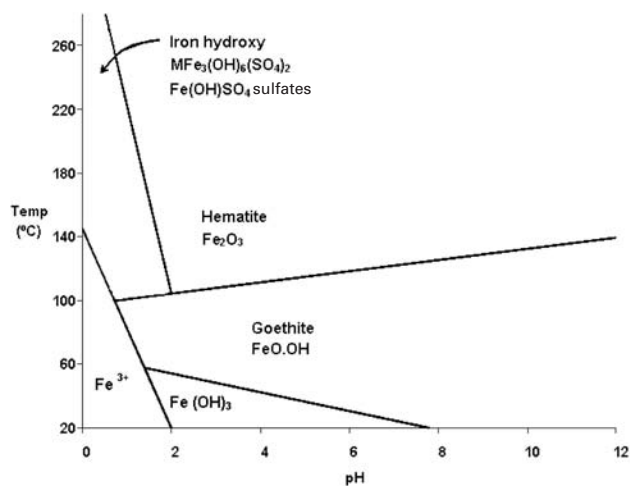


Figure 1 — Areas of stability of various compounds in the Fe-S-O system (after Babcan, 1971). Arrow indicates area of jarosite and basic iron sulfate stability.

tankage requirements, plant footprint and capital cost.

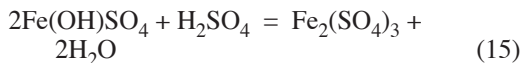
Although formation of the desired hematite and ferric arsenate hydrolysis products is favored at low acidities (< 20 g/L H_2SO_4) and high temperatures (> 200°C), in practice it is costly to operate an autoclave under conditions in which these are the dominant iron hydrolysis products in the solid phase. 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 preheat the feed, which also increases capital cost. Because of these significant capital cost considerations, commercial autoclaves are generally operated under conditions in which the formation of basic iron sulfate is a reality.

The “Hot Cure” process – the solution to the basic iron sulfate problem

The solution to the problems posed by basic iron sulfate formation is a simple one, and derives from the fact that the hydrolysis reaction that results in the formation of basic iron sulfate 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 temperature and pH is presented in Fig. 1.

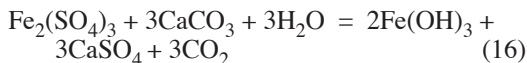
Although the area of stability for basic iron sulfate was not reported in the original publication (Babcan, 1971), it is assumed to be similar to jarosite, except diminished in size because of its lower stability. It can be seen from Fig. 1 that jarosite and basic iron sulfate will form under acidic conditions (pH < 2) and at high temperatures (> 140°C). It should also be apparent from Fig. 1 that jarosite and basic iron sulfate will break down under more strongly acidic conditions (pH < 1) and at lower temperatures (< 140°C), and this is the basis of the “Hot Cure” process (Ji et al., 2006). This acidic reaction

consumes acid and produces ferric sulfate in solution, and is the reverse of reactions (9), (10) and (11) for the formation of basic iron sulfate and jarosite:



It should also be clear from Fig. 1 that basic iron sulfate and jarosite will also break down under alkaline conditions ($\text{pH} > 2$) to form either hematite (at temperatures $> 100^\circ\text{C}$) or goethite (at moderate temperatures of 60° to 100°C). This is the basis of the Lime Boil process developed by Sherritt (Berezowsky and Weir, 1989), 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 drawback 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 sulfate, so requires no additional reagent and minor additional energy cost.

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



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

An added advantage of the Hot Cure process is that it allows the ferric sulfate 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 cyanidation, which mitigates their potential negative impact on rheology and mass transfer during gold leaching.

The gypsum and ferric hydroxide products of Eq. (16) would normally be sent to a thickener. The thickener underflow would join the tailings from the gold recovery operations for discharge to a common tailings facility and the thickener overflow would either be recycled to the plant as process water or treated for base metal recovery.

A simplified flowsheet for a refractory sulfide pressure oxidation/cyanidation process incorporating hot curing is shown in Fig. 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 four 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 Driefontein), to illustrate the potential impact of basic iron sulfate formation and the benefits

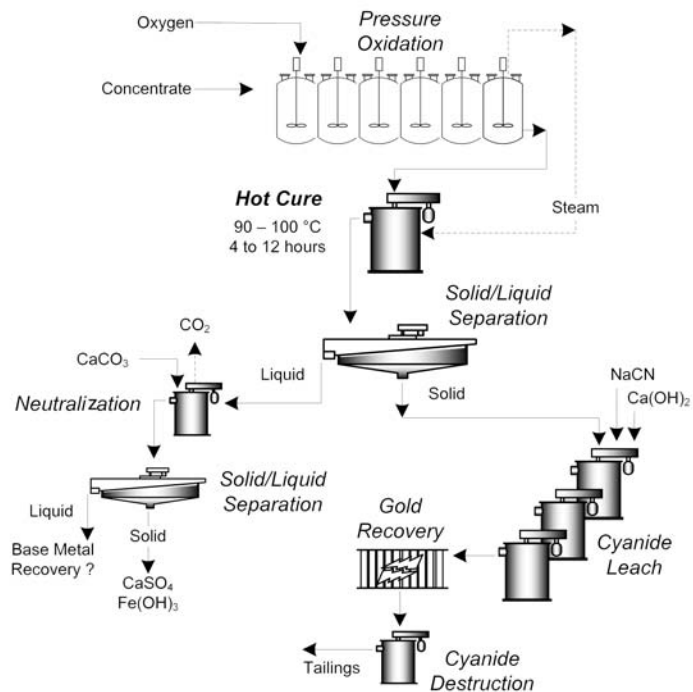


Figure 2 — Refractory gold pressure oxidation, hot curing and cyanidation flowsheet.

of the Hot Cure process.

The Quimsacocha project

The Quimsacocha project in Ecuador is owned by Iamgold Corporation. Gold is locked in a sulfide matrix consisting mainly of pyrite and enargite, and the flowsheet that is currently favored (at the prefeasibility stage) on technical and environmental grounds involves flotation to produce a bulk sulfide 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 favored 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 sulfate 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 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

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

Species	Feed Conc %	Test 1 Autoclave Only		Test 2 Autoclave + Hot Cure	
		Residue %	Solution g/L	Residue %	Solution g/L
Cu	1.38	0.007	1.72	0.007	1.75
As	0.47	0.33	0.13	0.10	0.55
Fe	24.0	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	1.20	na
[SO ₄] _{total}	0	20.0	72	2.9	100
H ₂ SO ₄	0	0	43	0	30

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, two-hour residence time).

The sulfate-to-iron ratio in the solid autoclave residue from the first test shows that the iron was converted from pyrite and enargite in the autoclave feed to predominantly basic iron sulfate in the residue. The theoretical mass ratio of sulfate-to-iron in basic iron sulfate (96/56) is 1.7, which means the sulfate 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 sulfate. 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 sulfate under optimum operating conditions, and less than 15% to hematite.

After hot curing, the sulfate content of the solids had decreased to 2.9% and iron to 3.6% and almost 90% of the original basic iron sulfate 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 sulfate. This portion could presumably have been reduced to zero under more aggressive hot curing conditions.

The rate of decomposition of the basic iron sulfate in the Quimsacocha autoclave residue is illustrated in Figs. 3 and 4. The data in Fig. 3 show the changing concentrations of

Fe and SO₄ in the solids as a function of time, and the mass ratio of the change ($\Delta SO_4/\Delta Fe$) is very close to the theoretical ratio of 1.7 that would be expected for basic iron sulfate. This confirms the 1:1 molar ratio for the formulation of basic iron sulfate {Fe(OH)SO₄} rather than a formulation such as that of hydronium jarosite {HFe₃(OH)₆(SO₄)₂}, which needs a Fe-to-SO₄ 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 sulfuric acid, as would be expected from Eq. (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 sulfate 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 sulfate in the latter solution (Eq. (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.

The washed solid residues from the two autoclave tests

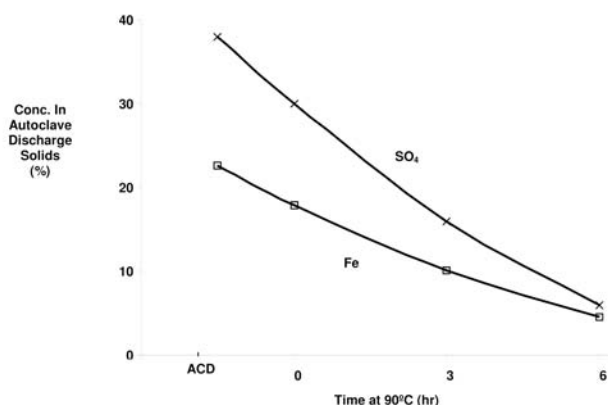


Figure 3 — Concentrations of iron and sulfate in the solids in the discharge from autoclaving Quimsacocha flotation concentrate, as a function of hot curing time.

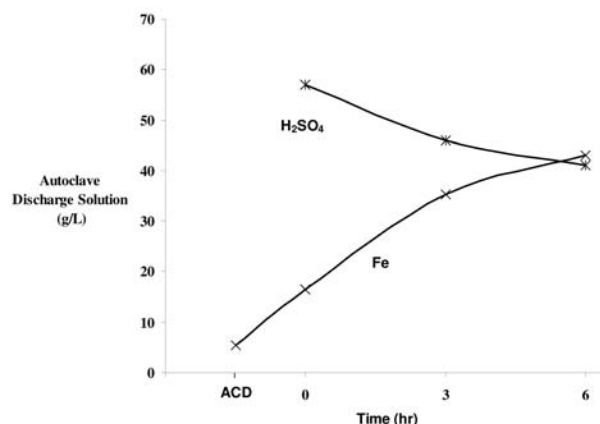


Figure 4 — Concentrations of iron and sulfuric acid in solution in the discharge from autoclaving Quimsacocha flotation concentrate, as a function of hot curing time.

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

	Units	Autoclave 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	10.0
Ag extracted	%	94.8	90.0
NaCN consumed	kg/t	1.75	2.92
Lime consumed	kg/t	213	18.9

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.

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 2000s 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 (Ji et al., 2006). 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 countercurrent decantation (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 sulfate was formed when Pueblo Viejo ore was pressure oxidized under optimum conditions (225°C, 100 psi oxygen, 60 minutes' residence time) than in the Quimsacocha project, because of the lower concentration of sulfide in the whole ore Pueblo Viejo autoclave feed (~4%) than the Quimsacocha concentrate autoclave feed (~20%). But even in this case, based on the sulfate (~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 sulfate under the optimum autoclave operating conditions, and very little to hematite.

The rate of decomposition of basic iron sulfate during hot curing of the pressure-oxidized Pueblo Viejo ore at 90°C is shown in Figs. 5 and 6. As predicted from Eq. (15), Fe and SO₄ in the solids decreased with time, as did sulfuric 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 (decreasing

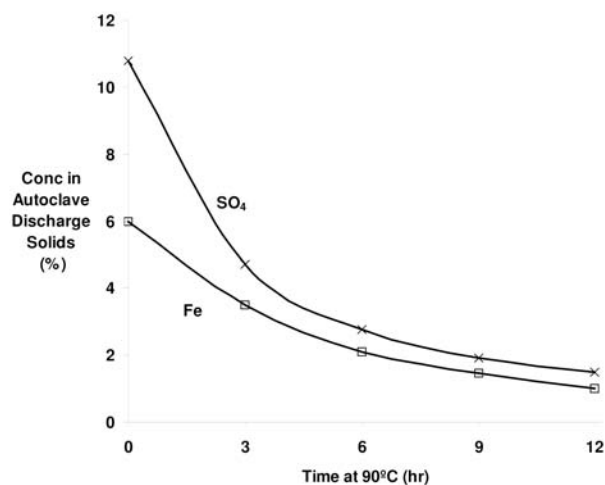


Figure 5 — Concentrations of iron and sulfate in the solid residue from autoclaving Pueblo Viejo ore, as a function of hot curing time.

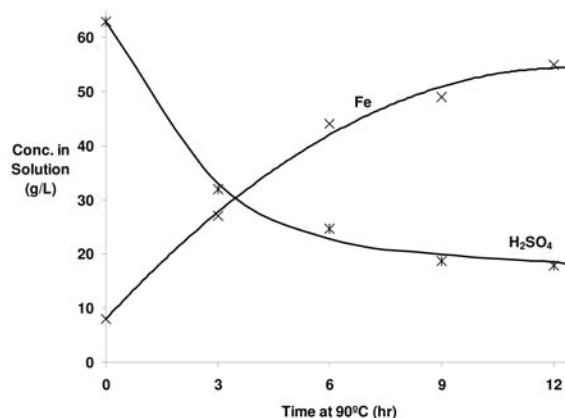


Figure 6 — Concentrations of iron and sulfuric acid in solution in the discharge from autoclaving Pueblo Viejo ore, as a function of hot curing time.

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

Product	Recovery		Alkali consumed		Approximate alkali cost
	Au%	Ag%	CaCO ₃ kg/t	Ca(OH) ₂ kg/t	\$/t
Autoclave discharge	96.7	78.5	110	62	10.50
Hot Cure discharge	96.3	3.5	195	8	3.20

from ~60kg/t to <10 kg/t), the savings in operating costs due to lower lime consumption would not have compensated for the loss of silver recovery (approximately 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 sulfate in the autoclave residue can be decomposed and washed from the solids prior to lime boiling. This step should significantly lower lime consumption in the Lime Boil process, which is its main negative feature.

Driefontein tailings retreatment 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 (Fleming et al., 2010).

In this case, one of the objectives of the autoclave process was to produce as much ferric ion as possible, to oxidize uranium

(IV) in the recombined rougher concentrate to U(VI), and as much sulfuric acid as possible, to react with acid-consuming gangue in the cleaner tails and solubilize the uranium.

To determine the influence of autoclave temperature and hot curing on the distribution of sulfate between sulfuric acid, ferric sulfate and basic iron sulfate, 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 sulfate and hematite was also examined.

The concentrate contained 17.4% Fe and 15% S²⁻, and the pressure oxidation tests were conducted at a pulp density of 15% solids. All of the sulfide in the concentrate was fully oxidized (>99%) to sulfate, in all three tests, and this would theoretically have generated 450 kg SO₄ 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.

The autoclave solution was analyzed for sulfuric acid and Fe, and the residue was analyzed for Fe and SO₄, 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 sulfate and ferric sulfate) and the distribution of sulfate between its three autoclave products (sulfuric acid, ferric sulfate and

Table 4 — Effect of autoclave temperature during oxidation of a pyrite concentrate on the concentrations of sulfate and iron products in the autoclave and Hot Cure discharge.

Temp °C	Concentrations in solution (g/L)				Concentration in the solids (%)			
	H ₂ SO ₄		Fe ₂ (SO ₄) ₃		SO ₄		Fe	
	ACD	HCD	ACD	HCD*	ACD	HCD*	ACD	HCD*
190	49	40	7.0	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	19.0	14.6

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

Table 5 — Effect of autoclave temperature during oxidation of a pyrite concentrate on the distribution of iron and sulfate in the autoclave discharge.

Temp °C	Fe distribution in ACD			Sulfate concentration (kg/t)							
	Hem %	BFS %	FS %	H ₂ SO 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 sulfate; FS = ferric sulfate; * Corrected for ~20% mass loss in hot curing

basic iron sulfate) are shown in Table 5.

The following can be concluded from the results in Table 5:

- The amount of sulfate analyzed in the autoclave products ranged from 420 to 460 kg sulfate per ton of concentrate in the three 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 sulfate (20 to 30%), with only about 10% in solution as ferric sulfate.
- The proportion of hematite increased with increasing temperature, as expected, whilst both basic ferric sulfate and ferric sulfate decreased with temperature. Distributions after hot curing are not shown, but the data suggested that ~90% of the basic iron sulfate decomposed to ferric sulfate during hot curing and there was no change in the amount of hematite (after correction for mass lost in hot curing).
- Most of the sulfate was converted to sulfuric acid (50 to 70%), and the percentage conversion increased with temperature from ~50% at 190°C to 70% at 230°C. Ferric sulfate accounted for 10 to 20% of the sulfate in the autoclave discharge and 20 to 40% in the Hot Cure discharge. Basic iron sulfate accounted for ~20% of the sulfate in the autoclave discharge, and >90% of it decomposed to ferric sulfate in solution during hot curing. The proportions of both ferric sulfate in solution and basic iron sulfate in the residue decreased with increasing autoclave temperature.

Conclusions

Basic iron sulfate is the product of a hydrolysis reaction that occurs when pyrite and other iron sulfide minerals are oxidized to ferric sulfate and sulfuric acid in an autoclave. The proportion of iron in the autoclave feed that is converted to basic iron sulfate increases with increasing ferric ion and sulfuric 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 favored at lower acidity in the autoclave solution (10 - 20 g/L) and higher temperatures (> 200°C). In practice, the production of a hematite residue with minimal basic iron sulfate is difficult to achieve without a significant capital cost penalty, and the formation of basic iron sulfate is a reality in all commercial autoclave operations. While 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 sulfate 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). It is only moderately stable under atmospheric conditions and can be decomposed both under alkaline conditions, which convert it to ferric hydroxide and gypsum precipitates, and acidic conditions, which convert it to ferric sulfate in solution.

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

keep cyanide in free cyanide form rather than the toxic, gaseous HCN form. The pH constantly drifts downward, due to the slow consumption of lime by basic iron sulfate, which leads to the formation of HCN gas and creates an unsafe working environment for gold plant operators.

One option is to neutralize the residue with lime at pH >10 prior to cyanidation, to convert the basic iron sulfate 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 fine precipitates.

The much-preferred option is to break down the basic iron sulfate under acidic conditions in the Hot Cure process. This process is somewhat faster (typically six to 12 hours) than high pH neutralization, requires no additional reagents and most importantly, allows all the iron and acid associated with basic iron sulfate 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.

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 quite 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 sulfate 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.

Acknowledgments

The permission from senior management of Barrick Gold Corporation, Iamgold and Goldfields Corporation to publish data from their projects is gratefully acknowledged.

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