

# Understanding Cyanidation of Silver from Batch and Continuous Medium Temperature Pressure Oxidation Generated Residues



R. T. Seaman and K. Mayhew

**Abstract** Pressure oxidative treatment of whole ores and/or mineral concentrates is used to leach or liberate metals of value for downstream recovery. Silver, when present, is often lost in processing, precipitating as a cyanide-insoluble jarosite in the residue. Depending on pressure oxidation conditions, the degree of silver loss to jarosite can vary dramatically. Batch bench-scale testwork is often performed to define that loss, and then assess the implications in continuous operations. This paper focusses specifically on the impact of CESL pressure oxidation conditions on silver recovery, and discusses limitations of batch bench-scale testing as well as means of overcoming these limitations to better predict silver recovery in the scale up from bench-scale to continuous operations. Since silver is only partially soluble in both sulphate and chloride media, it will gradually leach and deport to a jarosite as oxidation progresses. When a silver-insoluble anion, for example iodide, is dosed prior to oxidation, there is a marked improvement in silver recovery from batch-generated residue; however, that benefit is not consistently seen in continuous operations. The difference has been attributed to the dynamic solution conditions in the batch test, specifically the first few moments of oxidation. Using these principles, a predictive correlation has been established between initial leach concentrations of iron and acid and ultimate silver recovery with iodide addition.

**Keywords** Silver • Jarosite • Pressure oxidation • Cyanidation  
Iodide • CESL • Batch • Continuous

## Introduction

The formation of silver jarosite from ores and concentrates during medium temperature (110–150 °C) pressure oxidation is well known, as is the use of iodide during pressure oxidation to stabilize silver in a cyanide leachable form for

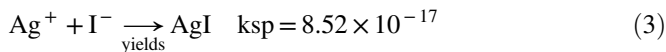
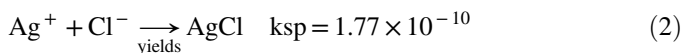
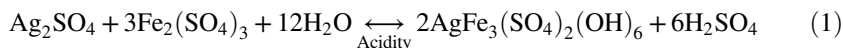
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subsequent processing [1]. The reactions for the precipitation of silver under medium temperature CESL oxidation conditions in a sulphate solution in the presence of chloride and iodide are presented below:

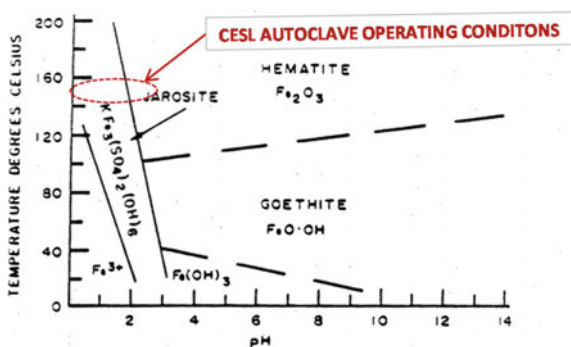


Based on Eq. 1, jarosite will form if silver and iron are in a mildly acidic solution. If the acidity were to increase significantly the jarosite formation could be impeded or reversed by the presence of excess sulphuric acid in the system. Figure 1 presents a generic phase diagram for stable iron species in a sulphate system.

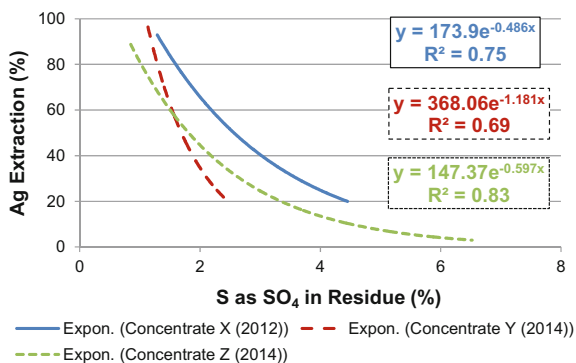
The CESL Process pressure oxidation step operates at 150 °C and 1380 kPag in sulphate and chloride media. The presence of chlorides and operation at medium temperature leaves most sulphur in sulphides as elemental sulphur in the residue after oxidation. Depending on the mineralogy of the concentrate processed, the pH of the final oxidation leach liquor can range from 0.5 to 3.0, represented by the red circle in Fig. 1. When the pressure oxidation step is performed in such a manner as to produce a higher pH discharge slurry, the subsequent cyanidation of that leach residue achieves typically >90% silver recovery.

Processing concentrates containing minerals that generate high amounts of acid, like enargite and pyrite, shift CESL pressure oxidation operations into a region where silver jarosite formation is favored. Figure 2 presents silver extraction versus jarosite formation data from pressure oxidation residues produced from batch bench-scale autoclave testwork in which no iodide was added and acidity was varied during the oxidation step. Sulphur as sulphate measured in the residue was used to infer relative jarosite formation. Slightly increasing acidity during the oxidation step corresponded to increased jarosite content in the residue and correlated with significant silver losses during cyanide leaching of those oxides.

**Fig. 1** Area of stability of various iron compounds in Fe-S-O system at 20–200 °C (Babcan 1971)



**Fig. 2** Silver extraction from CESL generated residues with varying sulphate content



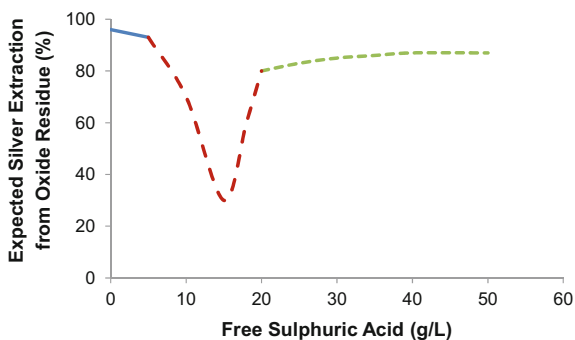
Assuming silver jarosite was the cause of poor silver extraction, the areas of iron stability as presented in Fig. 1 were used to define regimes for expected iron precipitates. In this paper, concentrates tested contained significant arsenic which potentially introduced iron-arsenic precipitate phases that are not included in Fig. 1. The major iron species precipitated at various CESL Process pressure oxidation solution acidities are presented in Table 1.

Note that iron arsenate formation was assumed stable for all acidities and that jarosite was hypothesized to be unstable at 150 °C and high acidity (>0.5 pH). Based on the free acid range for theoretical formation of jarosite reported in Table 1, a theoretical extraction correlation was generated to predict silver extraction results from these residues, as shown in Fig. 3. The solid blue line indicates the low acid, the wide dashed red line indicates medium acid, and the tight dashed green line indicates high and very high acid regimes as defined by Free Sulphuric Acid (FSA—defined in Eq. 4) in the pressure oxidation filtrate.

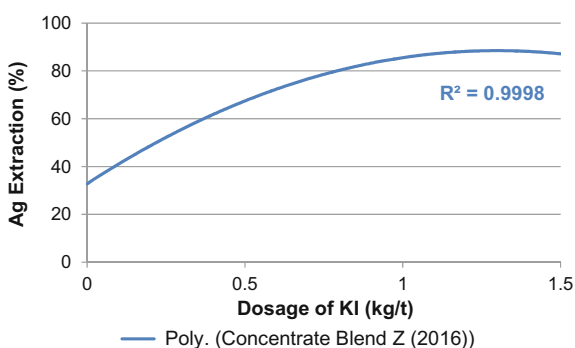
**Table 1** Pressure oxidation Free Acid (FA) regimes and assumed stable iron precipitates

Pressure oxidation solution conditions	Iron stability acid regimes	Theoretical type of iron precipitated
FA < 5 g/L	Low acidity	FeAsO <sub>4</sub> (Scorodite)
		Fe <sub>1-x</sub> AsO <sub>4</sub> (SO <sub>4</sub> ) <sub>x</sub> (OH) <sub>x</sub> [2] (BFAS II)
		Fe <sub>2</sub> O <sub>3</sub>
5 g/L < FA < 20 g/L	Medium acidity	Scorodite/BFAS II
		Jarosite (Ag)
FA > 20 g/L Fe and SO <sub>4</sub> not saturated	High acidity	Scorodite/BFAS II
FA > 50 g/L Fe and SO <sub>4</sub> saturated	Very high acidity	Scorodite/BFAS II
		Fe(SO <sub>4</sub> )(OH)

**Fig. 3** Theoretical silver extraction from CESL oxide residues



**Fig. 4** Silver extraction from CESL generated residue with potassium iodide additions



$$\text{Free Sulphuric Acid (FSA)} = [\text{FA}]_{\text{g/L}} - [\text{As}]_{\text{g/L}} * \frac{98 \frac{\text{g}_{\text{H}_2\text{SO}_4}}{\text{mol}}}{75 \frac{\text{g}_{\text{As}}}{\text{mol}}} * 1.5 \frac{\text{molH}^+_{\text{ArsenicAcid}}}{\text{molH}^+_{\text{SulphuricAcid}}} \quad (4)$$

Addition of iodide as potassium iodide prior to oxidation improved silver extraction from batch bench-scale generated oxide residues as seen in Fig. 4. This trend of improved silver recovery from iodide dosed concentrates during CESL batch bench-scale pressure oxidation testwork was seen with other concentrates operating in the medium acidity regime, and was considered to offer an economic means of enhancing silver recovery by suppressing silver jarosite formation. Therefore, when continuous pilot operations began in 2016, iodide dosing was employed, and as this paper will explain, did not perform as expected.

## Experimental

Data presented in this report originates from batch and continuous testing of several commercially available arsenic bearing copper concentrates and calcines for the purpose of performing an economic study on a custom copper refinery using the

**Table 2** Blends tested

Blends	Feed characteristic	Silver content (g/t)	Oxidation acid regime
1	Slightly acid generating	395	Medium acid with Iodide
2	Slightly acid generating	327	Medium acid with Iodide
3	Acid consuming	550	Low acid with Iodide
4	Greatly acid generating	104	medium acid with iodide
5	Slightly acid generating	351	Medium acid with iodide
6	Same feed as Blend 4	121	High acid with and without iodide
7	Same feed as Blend 2	339	Medium-high acid with iodide
8	Same feed as Blend 2	339	High acid with iodide

CESL Process. Concentrates were blended and acid conditions varied to assess optimal economics. Feed materials and conditions were held constant for one to three weeks of continuous pilot operations (24 h, 5 days a week) to assess each economic case, referred to as Blends. Eight Blends were trialed with feed material and operating conditions relevant to this paper summarized in Table 2.

Acid generating concentrates are defined as concentrates that generate pressure oxidation discharge solution that contains more acid and iron than was present in the feed. Acid consuming concentrates produce pressure oxidation discharge solution with less acid and iron than the feed. Blends 4 and 6 were performed on concentrate from the same mine and year; however, they were not homogenized prior to generating each Blend. As a result they reported slightly different head grades for silver; this is similarly the reason for the difference in the silver head grades between Blend 2 with Blends 7 and 8. The similar feed Blends were assumed to have identical mineralogy. Silver speciation in the concentrate was not performed, however silver was assumed to be a mix of mostly silver sulphide and some electrum both of which were significantly disseminated in the pyrite and enargite grains.

During each Pilot Blend operations, a feed concentrate, an acid feed and a pressure oxidation discharge sample were taken once steady state was achieved. Batch bench-scale tests were performed on the concentrate samples using the same conditions as in the continuous pilot plant operations, including the acid feed solution. These comparison tests were used to assess pilot copper extraction performance. The oxide residue from both the batch bench-scale testwork and continuous pilot operations were cyanide leached to compare relative silver extractions. Post campaign, kinetic batch testing was performed repeating Blends 2 and 8 to compare batch timed samples to continuous compartment samples to better understand the dynamic differences inherent for each test method and the impact on silver extraction from those residues.

All residues, continuous or batch generated, were cyanide leached in a 1 L Parr stainless steel operating at 500 psig O<sub>2</sub> at ambient temperature for 90 min with sufficient free cyanide levels. CESL residues contain a high fraction of elemental

sulphur, which can consume cyanide. Elevated oxygen pressure was used in the cyanidation step to increase precious metal cyanide leaching kinetics and reduce cyanide losses.

Silver extraction was based on silver assayed in the feed residue from the copper plant and in the final cyanidation residue. Silver in solids was determined through aqua regia digestion and atomic absorption. Free acid was calculated using the standard free acid titration (1 molar NaOH titrated to pH 3), and then FSA was calculated using Eq. 4. Arsenic was measured in solution using ICPMS and assumed to be present as arsenic acid. Finally, sulphur as sulphate was determined by performing a 10% v/v HCl digestion on the oxide residue followed by ICPMS analysis. Elemental or sulphide sulphur was assumed not to have leached using this technique.

## Results and Discussion

Table 3 presents the silver extraction from iodide dosed residues generated from continuous and batch operations using the same feed material and operating conditions. Compartment 1 and discharge acidity, in terms of free sulphuric acid (FSA), are reported as well.

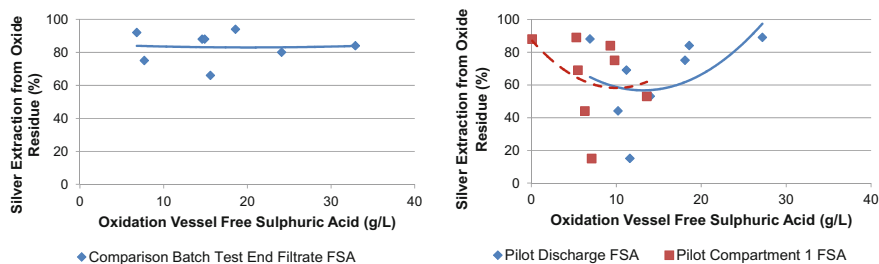
Plots of the silver extraction achieved from bench and pilot generated residues against the pressure oxidation filtrate free sulphuric acidity as reported in Table 3 are shown in Fig. 5.

The silver extraction achieved from batch comparison tests reported the expected silver extraction from iodide dosed tests as seen in earlier batch testwork, Fig. 4.

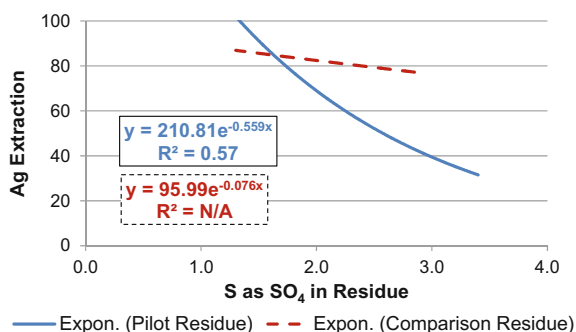
**Table 3** Oxidation acidity and subsequent silver extraction from batch and continuous generated residues

Blend	Acid feed	Batch (bench-scale)		Continuous (pilot-scale)		
		Discharge solution	Silver extraction	Compartment 1	Discharge solution	Silver extraction
	g/L FSA	g/L FSA	%	g/L FSA	g/L FSA	%
1	8.9	14.6	88	6.3	10.2	44
2	9.4	15.6	66	7.1	11.6	15
3	8.4	6.8	92	0.1	6.9	88
4	9.7	14.9	88	13.6	14.0	53
5	9.2	18.6	94	5.5	11.2	69
6 <sup>a</sup>	34.6	32.9	84	5.3	27.2	89
7	35.5	7.7	75	9.8	18.1	73
8	45.7	24.1	80	9.3	18.6	84

<sup>a</sup>Batch test was performed with synthetic acid make up



**Fig. 5** Silver extraction from batch residue versus the batch final filtrate FSA (L); Silver extraction from pilot residue versus compartment 1 and pressure vessel discharge FSA (R)



**Fig. 6** Silver extraction from continuous and comparison batch residues versus sulphur as sulphate in residue

The pilot continuous residue appeared to behave as if no iodide were dosed and followed the theoretical silver extraction curve hypothesized in Fig. 3.

A plot of silver extraction versus jarosite in residue represented as sulphur as sulphate for the tests presented in Table 4 is shown in Fig. 6. Despite continuous and batch residues reporting similar amounts of jarosite, batch-produced residue consistently reported higher silver extraction. Since the addition of iodide did not reduce the production of jarosite for either batch or continuous systems, there must be an intrinsic difference in the interaction of silver and iodide between the two methods.

**Table 4** Batch and continuous acidity and silver extraction values

Test		Acid feed	First minute	Compartment 1	Discharge	Silver extraction
		FSA g/L	FSA g/L	FSA g/L	FSA g/L	%
Blend 2	Batch	7.7	<0.1	10.2 <sup>a</sup>	14.6	93
	Continuous	9.6	6.0	6.0	11.9	38
Blend 8	Batch	43.4	39.3	7.8 <sup>a</sup>	<0.1	77
	Continuous	45.2	9.3	9.3	22.0	84

<sup>a</sup>Calculated using the weighted average from the kinetic samples for the first 25 min of the leach (~ retention time of Compartment 1 in Pilot)

To better understand potential differences, batch kinetic testwork was performed focusing primarily on the initial moments of oxidation with samples taken several times in the first 10 min. Kinetic tests were designed to match the feed and conditions from specific operation dates during the continuous operations so to make better comparisons. Blends 2 and 8 operation dates were selected to assess how filtrate acidity was changing during oxidation, presented in Figs. 7 and 8.

Free sulphuric acid values measured at times of interest from the figures above as well as the corresponding silver recovery from each generated residue are reported in Table 4.

Each test was equivalently dosed with iodide prior to oxidation. The batch test figures report a heat up period which represents the time when concentrate and acid feed were in anaerobic contact while the vessel was externally heated to target temperature. Time zero indicates when oxygen was introduced. Although heat up did slightly change the free acid, iron and arsenic solution tenors before oxygen introduction, previous acid injection testwork in which acid was injected after oxygen sparging showed no change in the subsequent silver extraction. The shaded area in Figs. 7 and 8 correspond to the same time slurry would have been held up in compartment 1 if processed continuously in the pilot vessel. The weighted average for free sulphuric acid in that period was compared to the compartment 1 values in Table 4.

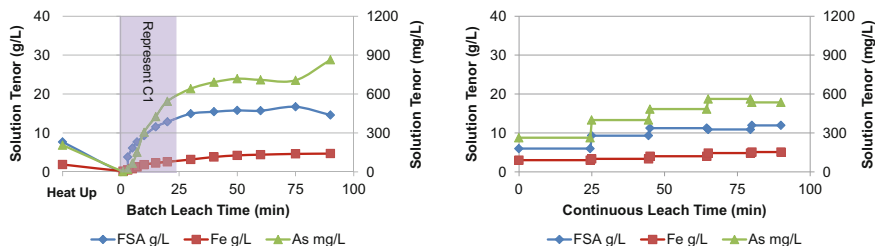


Fig. 7 Blend 2 batch kinetic (L) and continuous compartment (R) solution tenors versus oxidation time

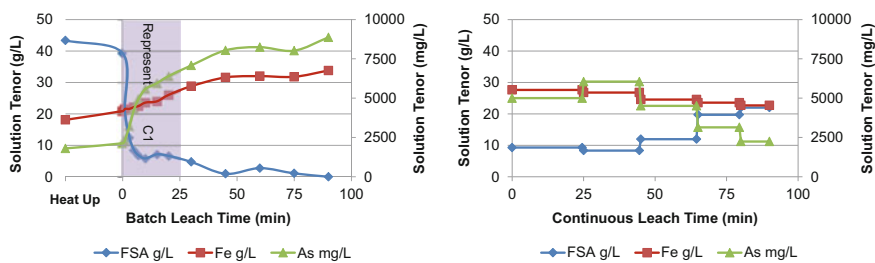


Fig. 8 Blend 8 batch kinetic (L) and continuous compartment (R) solution tenors versus oxidation time



Looking specifically at Fig. 7 and Table 4 to compare Blend 2 batch and continuous conditions, we see significant difference in the free sulphuric acid and iron concentrations as measured in the first minute. Referring back to Table 1, the batch test free sulphuric acidity of  $<0.1$  g/L would support both hematite and iron arsenate precipitation. These favored reactions would keep the iron concentration low and prevent the formation of silver jarosite (reaction 1). Conversely, the free sulfuric acid and iron concentrations present in the first minute of oxidation in the pilot compartment 1 during continuous operations supports silver jarosite formation. It is hypothesized that the brief moments of low acidity ( $<5$  g/L FSA) during the initial minutes of the batch test allowed iodide to interact with leached silver without competition. This allowed the formation of insoluble silver iodide (reaction 3) that kept the silver in residue for the duration of the leach. In the continuous system, iodide had to compete with jarosite for silver in the first minute, where iron and sulphate concentrations were ten times more abundant than iodide.

Follow up testwork demonstrated silver dosed as silver iodide and oxidized under jarosite forming conditions (from start to finish of the oxidation step) was almost entirely extractable in subsequent cyanidation.

Now consider Fig. 8 and Table 4 to compare Blend 8 batch and continuous conditions. The conditions in the first minute were very different. The first minute of oxidation in the batch test reported high free sulphuric acid conditions suppressing jarosite formation [3] and allowing silver iodide precipitation to occur with minimal competition. The continuous system reported medium acid conditions which supported jarosite formation. Based on the initial free sulphuric acidity for each test, one would expect good silver extraction from the batch test and poor extraction from the continuous system. Interestingly, residues from both tests reported similar silver extractions,  $>75\%$  suggesting that more than just the initial moments of oxidation influenced final silver deportment.

Continuing with Blend 8, the discharge pH for both the batch and continuous slurries were comparable at 0.6; however, the batch tests acidity was almost entirely held by arsenic acid. The continuous system discharged  $>20$  g/L FSA which should have been enough sulphuric acid to suppress jarosite formation as indicated from previous continuous pilot operations, Fig. 5. Theoretically, the formation of jarosite would have already happened in compartment 1, so the question remains: 'Why would the discharge solution at  $>20$  g/L FSA change the form of silver in the final residue?' Literature review has shown jarosite formation can be inhibited at higher acidities; perhaps it can be reverted once formed if the conditions support that equilibrium?

Overall, the effectiveness of iodide depended on the filtrate conditions of both the initial and final moments of the oxidation and what the most stable iron species would be at those conditions. Often acid consuming minerals are the fastest to be leached during pressure oxidation and in the case of batch tests this typically leads to low free sulphuric acid conditions in the first moments. This batch bias allowed silver and iodide to react without competition. In the case of batch tests in which more acid was dosed to achieve a high free sulphuric acid final concentration, any silver jarosite initially formed could hypothetically destabilize once high acidity

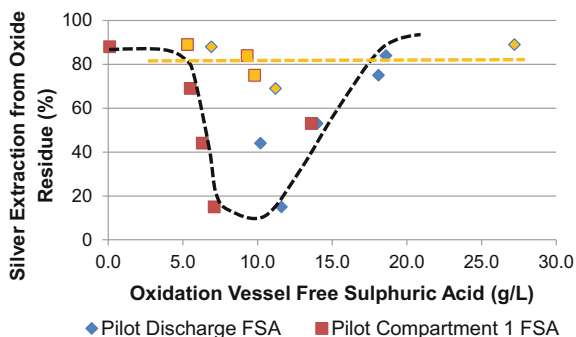
was reached allowing the iodide to slowly revert silver jarosite and allow for silver iodide formation. Based on this theory, batch tests ending in high acid would never achieve the same degree of silver extraction as low acid conditioned tests because the silver jarosite formed would inevitably leave some un-leached silver jarosite at the end of the oxidation. This limited maximum silver recovery from high acid generated residues is supported by the recoveries reported in Table 4.

Figure 6 depicts two sets of data from continuous leach trials: compartment 1 and autoclave discharge versus silver extraction from the generate residues. Figure 9 includes these data sets and highlights those points that had low acid in compartment 1 or ended in high acid. All the yellow highlighted data was treated as one data set and showed a silver extraction trend in solid yellow that followed the original batch comparison test results. Similarly, when all the non-highlighted data was treated as one data set, it reported the same theoretical silver extraction trend expected from non-iodide treated concentrates as in Fig. 3.

Figure 9 shows a greater definition for acid regime boundaries, where free sulfuric acid greater than 6 g/L in Compartment 1 appears to show degradation in silver extraction from residue. Similarly, discharge free sulphuric acids as low as 18 g/L show silver extractions greater than 80% from generated residues. In reality, operations near those boundaries may produce inconsistent results due to competing equilibriums; however, they support the proposed theory.

Figure 9 warns of the danger of assuming batch outcomes from continuous systems when assessing iodide effectiveness in silver recovery from oxidation residues without considering the oxidation dynamic system. This is not to say that dosing iodide cannot be an effective tool for increasing silver recoveries in your hydrometallurgical plant; rules of thumb need to be considered during the batch bench testing phase to get the most for your bench-scale analysis. In general, acid consuming and slightly acid generating concentrates should be tested under conditions that will yield low acid conditions in compartment 1; while acid generating

**Fig. 9** Silver extraction from pilot residue versus compartment 1 and pressure vessel discharge free acid



concentrates should be operated with an intended high acid value in the discharge. Achieving that high level of acid in the discharge may prove challenging because iron in the concentrate acts as a buffer, maintaining medium acidity so long as there is leachable iron left in the residue. Arsenic in concentrate aids in acid generation through the precipitation of high acid stable ferric arsenates and could be used as a tool to achieve desired high acidity for these concentrates industrially.

As a final note, based on the incredibly fast kinetics of silver leaching and iodide precipitation, investigations are ongoing on whether initial batch kinetics can be mimicked industrially to better utilize iodide additions for acid generating concentrates in continuous systems.

## Conclusions

Based on the interpretation of these results a set of axioms are proposed to better understand silver behavior under medium temperature pressure oxidation conditions:

- Silver leaching is fast (assumed as silver sulphide), freeing silver in the first minutes of oxidation.
- Silver iodide formation is fast.
- Silver jarosite formation is faster than silver iodide formation under medium acidity conditions, when in medium acid regime.
- Silver iodide, once formed, will not be converted, even in medium acidity regimes.
- Silver jarosite formation can be reversed under high acid conditions; however, this reversal never reaches completion and will leave some silver trapped in jarosite.
- Effectiveness of iodide addition in continuous systems depends on:
  - Compartment 1 acidity (not medium acidity).
  - Discharge acidity (only high acidity).

Iodide dosed, batch generated medium temperature pressure oxidation residues have limitations with respect to predicting silver extraction from continuous operations when the testing ends in medium or high acid. These conditions are commonly present when the concentrate contains significant amounts of pyrite and/or enargite because of their tendency to generate acid under pressure oxidation conditions. Based on the results outlined in this paper, silver extraction from copper concentrates can be optimized for concentrates with a range of mineralogies by considering compartment 1 and final acidity conditions in the autoclave. In general, for optimal silver recovery pressure oxidation of acid generating concentrates should be performed with higher acid in the acid feed; conversely, acid consuming concentrates should be operated with lower acid in the acid feed.

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