

THE RECOVERY OF CESIUM SALTS FROM THE TARON DEPOSIT

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Keywords: Taron, Cesium, Acid, Alum

ABSTRACT

The Taron deposit in Argentina contains significant concentrates of cesium in a complex oxidized mineral assemblage associated with iron-arsenic-aluminum-manganese-silica mineralization. The recovery of cesium has been studied using sulfuric acid leaching with recovery of cesium as alum. The waste solution from cesium recovery is oxidized and neutralized to form stable iron - arsenate residues. The cesium alum is further treated to form high purity cesium hydroxide, which may be further processed to a range of cesium salts including cesium formate. The initial process developments for the Taron deposit are presented.

INTRODUCTION

The Taron project is located 160 km northwest of the city of Salta, Argentina. The property consists of five (5) Contiguous Mineral Tenures, approximating 8,179 hectares (83 Units) in area. The Tenures are registered to Cascadero Minerals S.A. (CMSA), which is 100% owned by Cascadero Minerals Corporation (CMC), a Canadian Company, which is 70% owned by Cascadero Copper Corporation (CCD) and 30 % owned by Regberg Ltd. (RB). CMC operates as a 70% CCD and 30% RB joint venture (GeoSim, 2017).

The project is at approximately 4,250 metres above sea level. The annual rainfall (in the summers) ranges from 200-400 mm. Mid-summer high temperatures range from 14-21 °C with overnight lows of 6 °C. Mid-winter temperatures range to -8 °C with extremes of -15 °C. The project location is shown in Figure 1.

The Taron deposit has been subjected to exploration through trenching and drilling (2017). The mineralization has been described as follows (GeoSim, 2017).

The main zone of +200 ppm cesium mineralization lies in the Core and North Zones which cover a 700x1500 metre area intermittently exposed over a vertical range of 80 to 100 metres. Within this zone, the average Cs grade based on the 2017 drill results is about 1400 ppm Cs. Rb is closely correlated with Cs and averages about 220 ppm.

A sample from trench 109WW was submitted to SGS Mineral Services for petrographic, XRD, and SEM study (Hamilton, 2005). The initial sample analyses ran 7% Mn, 5% As, and 2% Cs. The study concluded the following:

- Arsenate cements account for about 25% of the sample and Mn-oxyhydroxides another 5%.
- Mn reports as both Mn-oxyhydroxides and as a suite of Ca-Fe- and Ca-Mn-Arsenate hydrate minerals, probably wallkilldellite. Only about 15% of Mn reports as Ca-Mn-Arsenate in the sample.
- Remaining Mn reports mostly as cryptomelane in massive form as well as radiating, concentrically banded Mn-oxyhydroxides. Among these minerals, coronadite, hollandite, and romanechite have been confirmed by XRD.
- There is a complex suite of arsenate mineral present, ranging from ludlockite, wallkilldellite and its Fe-analogue as well as pharmacosiderite, and yukonite.
- Cs reports predominantly as a Cs-substituted pharmacosiderite at levels of up to 12% Cs in this phase. Mixtures of Cs-pharmacosiderite and other phases are also present and as a result, producing a pure Cs-pharmacosiderite concentrate is unlikely.



Figure 1 – Taron Project Location

CESIUM EXTRACTION AND PURIFICATION PROCESS

Overview

The goal of this study was to develop a hydrometallurgical process for the production of marketable cesium formate solution, on the laboratory scale, starting from a cesium mineral sample obtained from the Taron deposit.

Figure 2 shows a conceptual flow chart of the tested process. Each unit operation was tested (conditions shown) sequentially without recycle. Atmospheric sulfuric acid leaching at 90 °C was applied to dissolve the cesium and other valuable metals into solution. After leaching, aluminum sulfate was added to the PLS (Pregnant Leach Solution) which was then stored in a refrigerator for 7 days. Cesium precipitated out of solution in the form of impure aluminum cesium sulfate crystals (alum) during this period. Afterwards, the liquid phase was removed, and the cesium containing crystals were left to air dry. These crystals were re-dissolved in boiling water. The resultant solution was filtered and returned to the refrigerator for re-crystallization. This process purified the initially collected crystals. After another 10 days in the fridge, the solution was decanted, and the crystals were filtered from the solution. These purified aluminum cesium sulfate crystals were dissolved in water, and barium hydroxide was added in two stages with two-step filtrations. The addition of barium hydroxide to the dissolved cesium aluminum sulfate first precipitated the aluminum as hydroxide and second precipitated sulfate as barium sulfate. The remaining solution contained cesium hydroxide. Formic acid was then added to the collected solution producing cesium formate. The overall procedure had three stages: leaching and crystal formation, crystal purification, and cesium sulfate purification, and the corresponding recoveries of cesium were 94.7%, 99.9%, and 96.1%, respectively. This gives a total of 90.9% cesium recovery over the entire process assuming all wash solutions are recycled without cesium losses.

As depicted in Figure 2, all wash solutions and two of the residues (the barium sulfate and aluminum hydroxide residues) would be recycled in a commercial process. All wash solutions can be concentrated by heating and evaporation. All other solid residues generated during the process have low cesium content and therefore are not economically feasible to be returned to the leaching stage. It is envisioned that these solids would report to waste disposal after neutralization, however further experimentation would be required to confirm the makeup of the combined waste stream.

Sample Preparation

The Taron mineral sample from a 2009 drill hole (No 5) was received in four bags (part A, B, C and D) of different moisture content and weight. Samples were crushed and ground to a P80 of 100 μm . Table 1 provides a typical sample analysis. The cesium content of the sample was 4761 ppm or 0.476%. There is a significant concentration of As, Fe, Mn and SiO_2 in the material.

Table 1 – Typical Taron Sample Analysis

ELEMENTS. All values are ppm(wt).												
Ag	Al	As	Ba	Be	Bi	Ca	Cd	Ce	Co	Cr	Cs	
1	33500	40495	2506	5	<0.5	28600	7	34	111	177	4761	
Cu	Dy	Er	Eu	Fe	Ga	Gd	Hf	Ho	K	La	Li	
1483	3	2	1	67300	13	2	1	1	17800	17	52	
Lu	Mg	Mn	Mo	Na	Nb	Nd	Ni	P	Pb	Pr	Rb	
<0.1	4100	>10000	11	14300	8	15	126	3400	22	4	407	
S	Sb	Sc	Se	Sm	Sn	Sr	Ta	Tb	Te	Th	Ti	
<500	4	3	3	2	2	542	1	<0.1	2	5	2060	
Tl	Tm	U	V	W	Y	Yb	Zn	Zr	F			
2533	0	11	82	1	16	1	2173	32	635			
OXIDES and Loss on Ignition. All values are wt%.												
SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	MnO	TiO ₂	P ₂ O ₅	Cr ₂ O ₃	Ba	LOI
48.86	8.7	9.7	4.07	0.86	1.74	2.14	8.13	0.42	0.82	0.03	0.24	5.76

Leaching

Leaching was conducted in 2-liter jacketed and baffled glass reactors maintained at 95 °C. The reactors had condensers to minimize evaporative loss. In a typical experiment, 1700 mL of 250 g/L H₂SO₄ solution was charged to the reactor and heated. A 450 g Taron mineral sample was then added and leaching continued for 4 hours. Intermediate samples were sometimes taken from the reactor for kinetic analysis. The reactors were agitated at 1000 rpm with overhead impellers. The final slurry was vacuum filtered via Büchner funnels. The solids were washed and dried before analysis and wash solutions kept separate from primary filtrate for analysis and metallurgical accounting. The primary filtrate was filtered again with finer mesh filter paper to ensure a clear solution for downstream processing.

Aluminum Cesium Sulfate Primary Precipitation

The leachate from each test was collected and treated with aluminum sulfate solution to promote formation of aluminum cesium sulfate precipitates (alum). A typical addition was 4 grams of aluminum per liter added as aluminum sulfate powder (and well mixed with the solution). The solutions were placed in a fridge (4°C) and left to crystallize alum for one week. The supernatant was sampled for analysis and the solids removed from solution and air-dried.

The purification of the alum crystals was necessary. Approximately 25-30 g of alum were leached in 750 mL of water at 90 °C for one hour. Any remaining solids (containing Ca, Fe and As) were filtered. The filtrate and solids were collected for assay. The remaining filtrate was again placed in a fridge for 7-10 days. The purified alum crystals were then recovered by filtration and drying. Washing was not applied in order to avoid alum re-dissolution.

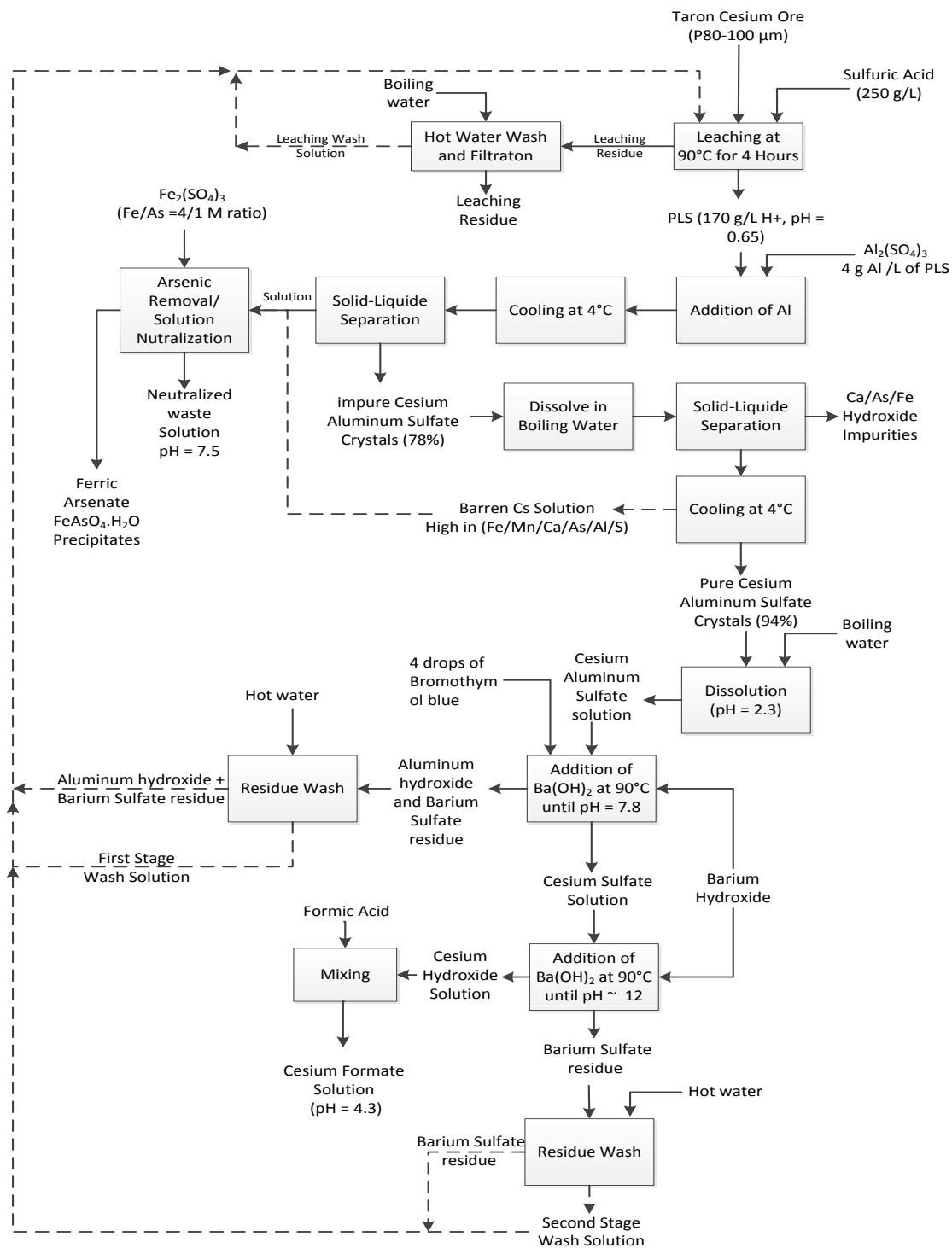
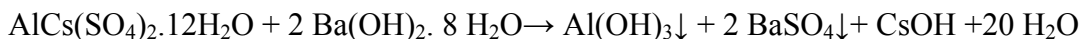


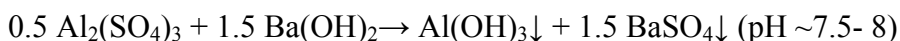
Figure 2 – Cesium Extraction Process. Dashed lines are potential recycle streams.

Cesium Hydroxide and Cesium Formate Production

A 2 g sample of the synthesized aluminum cesium sulfate crystals was fully dissolved in 100 mL of water held at 90 °C throughout the duration of the experiment. Barium hydroxide was added sequentially to a pH setpoint. All aluminum hydroxide and the majority of barium sulfate will precipitate at around pH 7.6 (bromothymol blue used as a pH indicator). Considering the overall precipitation reaction, 2 moles of barium hydroxide required per mole of aluminum cesium sulfate crystals assuming the following reaction goes to completion:

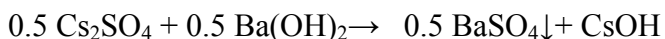


After each addition the pH, and the mass of remaining barium hydroxide was measured and recorded. When a pH of ~7.5 to 8 was reached, the addition of barium hydroxide was stopped. The first stage of the experiment stopped at this point to ensure the precipitated aluminum hydroxide didn't dissolve back into the solution after a further rise in pH. At this stage all aluminum hydroxide and 1.5 mole of barium sulfate should have precipitated as seen in the following equation:



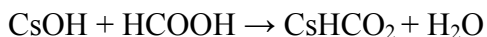
The slurry was then filtered of aluminum hydroxide and barium sulfate solids that had precipitated..

Barium hydroxide was then continually added to the solution and the pH of the solution was monitored after each addition. Barium hydroxide addition stopped when a pH of 11.83 was reached. It is expected that all barium sulfate precipitated at this pH according to following reaction:



This final pH of 11.8 was chosen as the end point for production of cesium hydroxide. Once the final pH was reached, the solution was filtered once again to remove the barium sulfate.

A further conversion of cesium hydroxide to cesium formate was performed. Formic acid was added in one to one stoichiometric ratio as shown in the equation below:



Arsenic Precipitation and Waste Treatment

Arsenic was removed from the PLS by first adding ferric sulfate at a 4:1 molar ratio of Fe^{3+} to As at 50°C, then adding calcium carbonate to precipitate ferric arsenate and raise the pH of solution.

EXPERIMENTAL RESULTS AND DISCUSSION

Leaching

The results of a typical leaching test are summarized in Table 2 below. The cesium extraction was excellent at 94.7% with high extractions of iron, arsenic and rubidium. The reported extraction was based on calculated head assays and the mass balance error relates to the comparison of the calculated and assay head.

Table 2 –Results for 4 hours of Leaching at 90 C with 250 g/L H₂SO₄ and 20 % Solids.

Element	Al	As	Cs	Fe	Rb	Tl
Extraction (%)	17.5	95.9	94.7	78.1	76.6	23.5
Mass Balance Error (%)	-4.9	9.9	8.5	7.0	1.4	4.1

Arsenic Precipitation before Cesium Recovery

A sample of leach solution was treated with iron (III) sulfate and limestone (CaCO₃) to precipitate arsenic as a ferric hydroxide/ferric arsenate precipitate. This was done with a 4:1 Fe/As ratio (mol/mol) for 4 hours at 50 °C. The results showed excellent precipitation of arsenic but the poor washing characteristics caused a loss of ~25% of the Cs with the precipitate. For this reason, the removal of arsenic by co-precipitation with iron is best performed after cesium recovery (as shown in Figure 2).

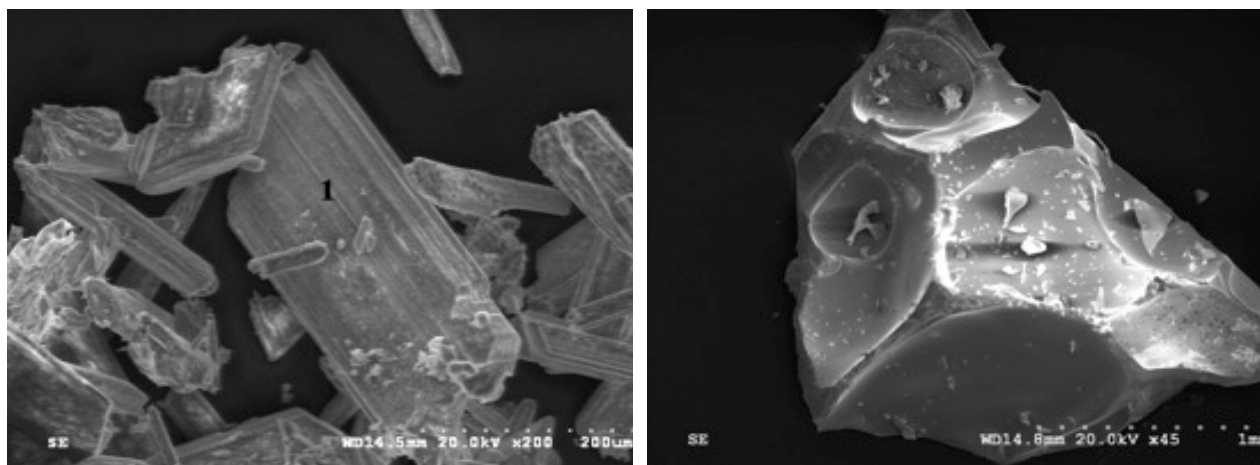
Aluminum Cesium Sulfate Precipitation and Purification

A series of experiments were performed to determine the requirement for aluminum addition to form aluminum cesium sulfate from the leachate. Additions of 2-8 g/L Al were tested with a further 7 days at 4 °C in a refrigerator to favour precipitation. These results are shown in Table 3.

Table 3 – Precipitation of Cs and Other Elements with Increasing Aluminum Sulfate Addition.

Addition/Precipitation (%)	Al	As	Cs	Fe	Rb	Tl
2 g/L Al	5.2	4.1	97.8	4.2	62.2	8.0
4 g/L Al	12.6	9.0	98.9	11.3	70.2	8.2
6 g/L Al	5.8	6.1	99.2	6.2	77.2	11.4
8 g/L Al	14.2	12.3	99.4	14.5	82.1	15.3

From this test it was confirmed that refrigeration of the samples after aluminum addition significantly increases the cesium and rubidium recoveries. The addition of 4 g/L aluminum was chosen for further testing because it produced 98.9% recovery of cesium as well as an adequate rubidium recovery. An SEM-EDX analysis of the precipitates formed after aluminum addition (cesium aluminum sulfate crystals and gypsum) is shown in Figures 3.



(a)

(b)

Figure 3 – SEM Pictures of (a) Gypsum and (b) Cesium Aluminum Sulfate Crystals

Analysis showed that the impure aluminum cesium sulfate crystal had a purity of 77.9% on a weight metal basis. After the purification process the purity on a weight metal basis increased to 94.2%. The purification results are summarized in Table 4.

Table 4 – Purification of Cesium Aluminum Sulfate Crystals

Crystal/Element (ppm)	As	Ca	Cu	Fe	Mg	Mn	P	Rb	S	Sr	Tl
Impure	9227	48100	241	23900	80	2170	80	6522	181000	589	133
Purified	24	<100	2.3	13400	<10	6	<10	1106	106000	7	7

Cesium Formate Production

The cesium aluminum sulfate was dissolved in water and purified in two steps as per the process description. The final cesium hydroxide solution was then treated with formic acid to make cesium formate solution.

The results of the purification are summarized in Table 5.

Table 5 – Cesium Hydroxide and Cesium Formate Solution Production

Stream/Element (ppm)	Cs	Al	S	Ca	Fe	K	Rb	Si
Alum Dissolution Solution	4885	902.3	2944	48.4	65	4	32.7	7.4
Cs Sulfate Solution (pH ~8)	6265	1	933	15	<10	7	35	4.6
Cs Hydroxide Solution (pH ~12)	7431	1	218	2	<10	11	43	22
Cs Formate Solution	7425	2	515	1	<10	9	42	20

Iron dropped from 65 ppm in the initial solution to undetectable amounts (<10 ppm) after the first filtration. Similarly, calcium levels dropped from 48.4 ppm in the initial solution to 0.9 ppm

in the final cesium formate solution commercial brines. Further testing is required to develop methods to concentrate and purify the final product solution.

CONCLUSIONS AND RECOMMENDATIONS

This study has covered the process development for the production of cesium formate from the Taron deposit using batch tests in the laboratory scale. Continuous tests on the laboratory scale and mini pilot scale (~1kg/h) are suggested before moving onto an industrial scale.

The investigation of alternative processing schemes for Taron mineralization will be presented in future publications.

REFERENCES

GeoSim Services Inc., TARON PROJECT NI 43-101 TECHNICAL REPORT, Salta Province, Argentina, September 14, 2017.