

Selenium impurity in sodium sulphate decahydrate formed by eutectic freeze crystallization of industrial waste brine

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Synopsis

Eutectic freeze crystallization (EFC) is a novel technique for the recovery of pure salt and pure water from hypersaline waste brines. It is therefore a promising technology for the treatment of industrial waste waters. The impurities caused by crystallizing salt out of multi-component brines by EFC have not yet been investigated, however. To these ends, the selenium impurity found in sodium sulphate, produced from the waste brine of a platinum operation, was investigated. It was believed that the similarity between sulphate and selenate ions allowed isomorphous substitution of selenate ions into the sodium sulphate crystals, which was the likely cause of impurity uptake. It was found that the presence of sodium chloride in the industrial brine promotes the uptake of selenium, while ionic strength of the brine and mass deposition rate of sodium sulphate did not have a significant effect on the selenium uptake. Isomorphous substitution is predicted to be the most significant mechanism by which all impurities will be taken up when applying EFC to other industrial waste brines.

eutectic freeze crystallization, impurity, salt, brine, sodium sulphate, waste water, isomorphous.

Introduction

Eutectic freeze crystallization (EFC) is a novel process for the treatment of hypersaline waste brines. Many industrial waste brines, especially those produced by the mining industry, contain a large variety of dissolved components. Some of these components are in quantities substantial enough to economically justify attempts at recovery in the form of salts, though in the past this has not been viable. With EFC, however, there is the potential to extract useable, pure salts and potable water while greatly reducing the volume of waste effluent.

There are a number of recent papers discussing EFC both as a means to recover salts (van der Ham, et al., 1997; van der Ham, et al., 1999) and how it can be specifically applied to the treatment of multicomponent hypersaline brines (Lewis, et al., 2010; Reddy, et al., 2010; Nathoo, et al., 2009; Randall, et al., 2010). This research has not yet investigated the impurities that are

encountered when crystallizing salts out of such complex brines. Because the feasibility of EFC is heavily invested in its capacity to recover useable salts, a better understanding of the salt purity is required.

Due to the large variety of industrial brines, it is not possible to perform comprehensive studies on all brines. Instead, by investigating a number of selected case studies, generalities and commonalities between brines and salt impurities can be found. In so doing, it will be possible to build up a library of predictable impurities that may be encountered when applying EFC to industrial waste brines. This work represents the beginning of such an investigation. In addition to discussing a case study where the salt purity of an EFC process was investigated, this paper will also highlight the general purity issues that can be expected from brine treatment with EFC.

Broadly speaking, the different ways in which impurities can occur in crystals are through liquid inclusions, isomorphous inclusions, and adhesions. Adhesions refer to surface impurities that can usually be removed by washing. Liquid inclusions are chambers of mother liquor that are entrapped by growing crystals. These liquid inclusions contain the impurities that existed in the mother liquor and cannot be removed by conventional washing. Isomorphous inclusions are ionic substitutions or solid solutions (Kirkova, et al., 1996). Sometimes when an impurity has a similar structure to one of the ions comprising the crystallizing salt, it can occupy a place in the lattice of the crystal. Liquid inclusions and adhesions have been found to have a negligible impact on the purity of the product salt when compared to isomorphous substitution (Zhang, et al., 1999).

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The purpose of this work is to re-evaluate a case study done by Reddy *et al.* (2009) with reference to the selenium impurity detected in the sodium sulphate product. The specific impurities found in this case study were not evaluated further, and it is believed that benefit can be had from a closer evaluation of the purity of the sodium sulphate product. Many waste brines from the South African mining industry contain large amounts of sodium sulphate, and the presence of selenium is common. In this way, this brine is representative of many South African brines. Investigating the nature of this selenium uptake will provide information into the feasibility of EFC application to similar brines. Additionally, this paper investigates generic mechanisms for the uptake of impurities in EFC.

Discussion of original case study results

The waste brine is produced by a platinum refining operation, and is typified by very high concentrations of sodium sulphate and sodium chloride. There are also a large number of other dissolved microcomponents. It has been found that the sodium sulphate produced from this brine contains appreciable amounts of selenium.

After the crystallization of sodium sulphate from the brine, it was found that Cl⁻, Se, and HCO₃⁻ were the main detected impurities (Figure 1). Reddy *et al.* (2009) believed the impurity to be a result of adsorption onto the surface of the sodium sulphate, but did not discuss the impurity further. While this proposed mechanism is not contested, there is little evidence in the literature to support adsorption under these circumstances. While it is possible that surface adsorption does occur during crystal growth, these impurities are likely to be incorporated into the crystal as it grows, to form a solid solution (Pina, 2012). This paper aims to further investigate these impurities, and other mechanisms by which they are taken up.

A common source of contamination is liquid inclusion and surface entrainment. From the analysis of the washing results, however, it can be deduced that liquid inclusions are not a significant source of impurity uptake. Figure 1 shows that the concentration of chloride decreased significantly after the first wash. This is due to the mother liquor being washed off the surface of the crystals, removing entrainment and

Table I						
Composition of platinum waste brine						
Species	mg/kg	Species	mg/kg			
Na	75756	Si	8			
CI	52889	Se	775			
Ni	14	Te	2			
K	256	Pt	3			
Ca	47	Pd	0			
Fe	0.2	Au	0.3			
Cd	0.3	Rh	0.4			
Li	36	Ru	2			
NO ₃ -N	2200	lr	0			
NH ₄ -N	1008	Ag	0.2			
CO ₃	0	В	0.9			
Mg	27	As	109			
SO ₄	72870	Р	8			
HCO ₃	3904					
Temperature	20°C	pH	9			

adhesions. Before washing, the total amount of chloride can be assumed to the sum of that from the liquid entrainment and that from the liquid inclusions. After the first wash, however, the chloride level decreased noticeably and the remaining chloride is what was assumed to be contained within the liquid inclusions only. Considering that the mother liquor contained a high concentration of dissolved chloride, it is expected that it would be the most abundant impurity resulting from liquid inclusions. When considering the total impurity in the salt, however, chloride is insignificant when compared to selenium. Selenium has a comparatively low concentration in the brine. If liquid inclusions or surface entrainment were the main source of impurity, the chloride concentration would be much higher than selenium. Liquid in inclusion is thus disregarded as a significant source of contamination

Figure 2 and Figure 3 suggest the likelihood of isomorphous substitution being the main source of selenium impurity. In order for liquid inclusions to be the main source of selenium impurity, the relative ratios of the impurities must be the same in both the mother liquor and the salt. Instead, a large amount of selenium was preferentially retained; this selenium impurity is therefore believed to be isomorphous in nature, though surface adsorption cannot be entirely disregarded at this stage.

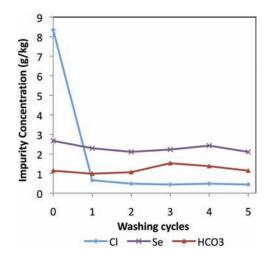


Figure 1—Concentration of impurities in salt after successive washing with saturated sodium sulphate (Reddy et al., 2009)

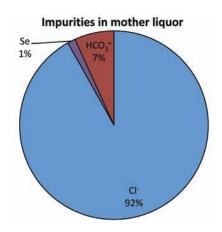


Figure 2-Mass ratio of non-crystallizing components in waste brine

Impurities in product salt

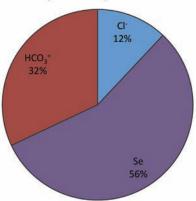


Figure 3—Mass ratio of major non-crystallizing components in salt from waste brine

To gain a better understanding of the nature of the preferential uptake of selenium, a number of investigations were conducted. The following experiments aim to better illustrate the likelihood of isomorphous substitution being the main mechanism of selenium uptake, as well as other factors that may promote the selenium impurity.

Materials and methods

Nature of selenium impurity - selenate or selenite

The two likely possibilities are that selenium is present in either selenite form (4^+ oxidation state) or selenate form (6^+ oxidation state). Due to the structural similarity between selenate and sulphate ions it was expected that the selenium is in the selenate form. The possibility that the selenium was present as selenite could not be ignored, however, and as such this possibility was also investigated.

A standard solution containing 90 g/ ℓ NaCl and 110 g/ ℓ Na₂SO₄ was made up. One batch was enough to supply all the individual beaker tests. Separate solutions containing 150 g/ ℓ Na₂SO₄ and 150 g/ ℓ Na₂SeO₃ were also made up. These were also enough to supply the entire experiment. All solutions were made with 18 M Ω .cm water.

200 m $_{\ell}$ of the NaCl/Na₂SO₄ solution was pipetted into each beaker. The necessary quantity of Na₂SeO₄ or Na₂SeO₃ was then pipetted into the beakers. The change in volume due to the addition of Na₂SeO₄ and Na₂SeO₃ was considered to be negligible since these constituted less than 1.5% of the total volume. Each individual beaker test was repeated three times. The concentrations of Na₂SeO₄ and Na₂SeO₃ can be found in Table II.

The beakers were then placed in a temperature-controlled room at -3.5°C and stirred with magnetic stirrers. For reasons of space and practicality, only six beakers were cooled at a time. The beakers were left at this temperature for 4 hours. At this point the salt from each beaker was filtered, and placed in an oven to dry. The purpose of the drying was to prevent analytical inaccuracies caused by the unpredictable decay of the decahydrate to the anhydrate form of sodium sulphate. The oven melts the sodium sulphate decahydrate and then drives off the water. In the absence of water and at

the higher temperature, all the sodium sulphate crystallizes in the anhydrous form. After the drying process the crystals were ground in a pestle and mortar and sent to be analysed externally by ICP-OES.

Thermodynamic modelling

In order to investigate if a separate selenium salt is being produced, it is necessary to thermodynamically model the system. This was done using OLI stream analyzer (OLI Systems Inc, 2008). A thermodynamic model was run, whereby a solution containing the dissolved species shown in Table III was cooled from 20°C to -10°C. The composition was chosen to represent the most significant dissolved species found in the waste brine.

Impact of ionic strength and common ion on uptake of selenium by sodium selenate

An additional factor suspected to have an impact on the uptake of selenium was the presence of excess sodium ions. This, as well as ionic strength, was investigated.

An experiment was conducted whereby the ionic strength of the mother liquor was altered and the resulting selenium impurity in the sodium sulphate product was measured. The ionic strength of the solution was increased by adding potassium chloride to a standard solution containing the same concentrations of sodium sulphate and sodium selenate as the original industrial brine. Potassium chloride was used so that the ionic strength of the solution could be adjusted without adding sodium to the solution.

In parallel to the above experiment, an identical experiment was performed whereby the ionic strength was increased by the addition of sodium chloride. In this way, a direct comparison could be made between the solutions containing sodium chloride and potassium chloride, to clarify the impact that the common sodium ion has on the uptake of selenium.

Table II

Concentrations of sodium selenate or sodium selenite in beaker tests

Batch		Sodium selenate (g/ℓ)	Sodium Selenite (g/ℓ)	
	1	1.00	1.00	
	2	1.30	1.30	
	3	1.60	1.60	
	4 5	1.90 2.20	1.90 2.20	
	J	2.20	2.20	

Table III

Concentration of components in simulated brine

Component		
		Concentration (g/t)
	Na ₂ SO ₄	110.6
	Na ₂ SO ₄ NaCl	87.1
	Na ₂ SeO ₄	1.9

A standard solution containing of 3.36 g/ ℓ Na₂SeO₄and 220 g/ ℓ Na₂SO₄ was made. Separate solutions containing 200 g/ ℓ NaCl and 200 g/ ℓ KCl were also made. All solutions were made with 18 M Ω .cm water.

100 m ℓ of the Na₂SO-₄/Na₂SeO-₄ was pipetted into each 250 m ℓ beaker. Then the necessary quantity of KCl or NaCl was pipetted into the beakers. 18 M Ω .cm water was used to top up each beaker to 200 m ℓ . Each individual beaker test was repeated three times. The concentrations of NaCl and KCl can be found in Table IV. Note that each concentration was done for both KCl and NaCl. Thus there was a total of 8 different compositions, each repeated 3 times, for a total of 24 runs.

After the samples were prepared they were placed in a temperature-controlled room at -3.5°C and stirred with magnetic stirrers. The beakers were left at this temperature for 4 hours. At this point the salt from each beaker was filtered, and placed in an oven to dry. The purpose of the drying is to prevent analytical inaccuracies caused by the unpredictable decay of the decahydrate to the anhydrate form of sodium sulphate. The oven melts the sodium sulphatedecahydrate and then drives off the water. In the absence of water and at the higher temperature, all sodium sulphate recrystallizes in the anhydrous form. After the drying process the crystals were ground in a pestle and mortar and sent to be analysed externally by ICP-OES.

Impact of mass deposition rate on the uptake of selenium

The last factor impacting on the uptake of selenium that was investigated was mass deposition rate. At higher mass deposition rates, it is more likely that foreign substances are accidently incorporated into the crystal lattice (Kirkova, *et al.*, 1996). This was investigated further.

In this experiment, sodium sulphate brine samples containing varying amounts of sodium selenate were cooled at different rates. The rate of mass deposition of sodium sulphate was calculated, as was the resulting selenium impurity for each run. In this way, it could be seen if there is a correlation between mass deposition rate and selenium uptake.

Synthetic brine was made up to simulate the major components of the platinum refinery waste brine, 90 g/ ℓ NaCl, and 108 g/ ℓ Na₂SO₄. To minimize variance within the experiment, one batch of synthetic brine was made to supply all individual runs.

Three separate runs were performed. In the first run, three brine samples containing 1.0 g/ ℓ , 1.6 g/ ℓ , and 2.2 g/ ℓ respectively were cooled from 20°C to -3°C over 24 hours. The samples were cooled in 200 m ℓ glass-jacketed crystallizers. The crystallizers were connected in series to a chiller,

Table IV				
Concentrations of	concentrations of NaCl or KCl in mother liquor			
Batch	Concentration (g/ℓ)			
1	70.00			
2	80.00			
3	90.00			
4	100.00			

circulating ethylene glycol as the coolant. In addition to being cooled by a chiller, the crystallizers were placed in a temperature-controlled room. The temperature of the room was dropped periodically to match that of the circulating glycol. The fact that the chillers were connected in series as opposed to parallel did not have a noticeable effect on the cooling rate of the brines. Every two hours, the temperature was measured and a sample of the supernatant liquid was taken. This information was used to calculate the rate of removal of sodium sulphate from the solution, and thus the deposition rate on the crystals. Once the brine was cooled for the full duration, the formed salt was filtered. To prevent inconsistencies resulting from incomplete washing, none of the samples were washed. After filtration, the salts were placed in an oven to dry. After the drying process, the crystals were ground in a pestle and mortar and sent to be analysed externally by ICP-OES. The second and third runs were identical to the first, except that the samples were cooled over 12 hours and 6 hours respectively.

Results and discussion

Selenite vs selenate

Figure 4 shows that selenate is taken up preferentially over selenite. Additionally, the selenate values are comparable to the results from the actual brine tests, whereas the selenite values are not. In the actual brine, a concentration of roughly 10 8 g/t of sodium sulphate, 90 g/t sodium chloride, and 775 mg/ℓ selenium produced an impurity of 2–3 g/kg of selenium in the product sodium sulphate salt. Though this result was not exactly matched in the experiment, it can be seen that the selenate values fall within the same orders of magnitude as the values found in the industrial brine. This discrepancy could possibly be attributed to all the selenium in the industrial brine not being in selenate form. In the experiments, all the selenium was present as selenate, whereas in the industrial brine, some selenium could have been present as selenite. As can been seen in the results, selenite does not contribute significantly to impurity uptake.

In addition to selenate and sulphate ions having similar structures, sodium sulphate and sodium selenate are isostructural (Balarew, 2002). It has been found that sodium sulphate decahydrate and sodium selenate decahydrate

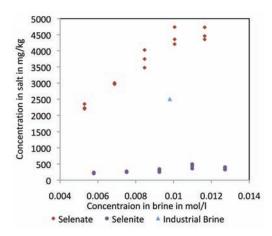


Figure 4—Comparison between uptake of selenate and selenite by sodium sulphate

readily form solid solutions within each other. This would indicate that there is minimal energetic disturbance to the crystal structure of one salt, if an ion from the other salt is substituted into it. It was also found that there is complete miscibility between sulphate and selenate ettringite (Hasset, et al., 1990). While these facts do not confirm that isomorphous substitution is the only source of contamination, they provide strong evidence that it is the most likely source of contamination.

These findings support the theory that the similar nature of selenate and sulphate ions is the main reason for the selenium inclusion. Because selenate results in a much greater impurity uptake than selenite, it can be concluded that in terms of impurity inclusion, the selenate ion is of greatest interest.

Impact of ionic strength

It can be seen in Figure 5 that increasing ionic strength does not have a significant impact on the uptake of selenium. This is illustrated in both cases, for NaCl and KCl. An increase in the concentration of sodium chloride did not show an increase in the uptake of selenium. It is possible that over a broader range, a change in the detected concentration of selenium in the sodium sulphate product might be noticed.

It can also be seen that the uptake of selenium is significantly increased by the presence of sodium chloride as opposed to potassium chloride. This indicates that it is specifically the presence of extra sodium that influences the degree to which selenium is taken up.

Likelihood of formation of separate salt

It can be seen in Figure 6 that no selenium salt is predicted. Selenium is present in small quantities, and the model does not predict that there are any selenium-based salts that would form under these conditions. It is therefore unlikely that the presence of selenium can be attributed to a separate

Results and discussion from mass deposition experiment

Figure 7–9 display the differing mass deposition rates for different sodium selenate concentrations and cooling rates.

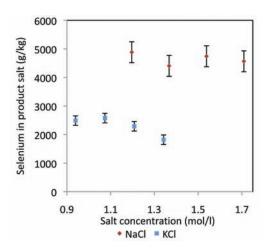


Figure 5-Impact of ionic strength on uptake of selenium by sodium

The units of the mass deposition rate are arbitrary. They are meant to compare the rate at which sodium sulphate is leaving solution and depositing on the salt. It must be noted that the temperature is a linear function of time. What can be seen for all experiments is that the mass deposition rate is mostly constant for each cooling rate over the length of the experiment. The average mass deposition rate for each experiment is summarized in Table V.

In addition to the mass deposition rates being relatively constant throughout each experiment, they were also consistent between the experiments (TableV). What can be inferred from this is that for each experiment, the rate of sodium sulphate deposition was constant throughout the experiment, and was comparable between analogous experiments.

Figure 10 shows the results for the uptake of selenium at differing mass deposition rates. From this data it cannot be said that mass deposition rate has a noticeable effect on the uptake of selenium. In the 1 g/ℓ experiments, the fastest deposition rate led to the greatest uptake of selenium, but the rate was only slightly more than the uptake at the slowest deposition rate. Overall, the second fastest deposition rate consistently resulted in the lowest uptake of selenium. Even if the data points are manipulated to limits of their error, they do not represent a situation where the uptake of selenium is definitively a function of mass deposition rate.

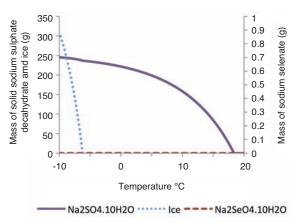


Figure 6 - Solids produced by simulation of cooling of 1 litre of synthetic brine. The concentrations of the components can be found in

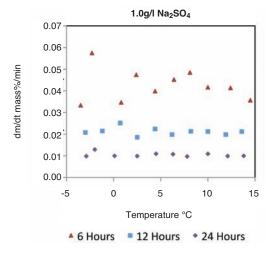


Figure 7—Mass deposition rate of 1.0 q/l sodium selenate brine samples at differing cooling rates

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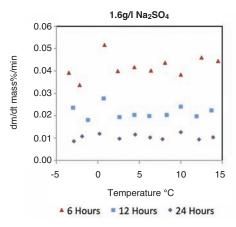


Figure 8—Mass deposition rate of 1.6 g/ ℓ sodium selenate brine samples at differing cooling rates

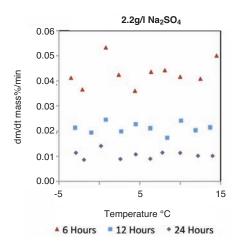


Figure 9—Mass deposition rate of 2.2 g/ ℓ sodium selenate brine samples at differing cooling rates

Table V					
Mass deposition rate for different cooling rates and sodium selenate concentrations in mass%/min					
Sodium selenate (g/ℓ)	1.0	1.6	2.2		
Cooling rate 1°C/hour 2°C/hour 4°C/hour	0.010 0.021 0.042	0.010 0.022 0.043	0.011 0.021 0.042		

In ionic crystals, the growth particles are subject to strong orienting forces (Myerson, 1977). The stronger these forces are, the more rapidly the depositing ions can be correctly positioned to be incorporated into the lattice. For the mass deposition rate to influence the uptake of impurity, deposition must be more rapid than the rate at which the ions can be correctly oriented and positioned. It is possible that rapid enough mass deposition to cause this to happen was not achieved. It is not likely, however, that the solution could be cooled more rapidly without substantial scaling of ice occurring. Industrial-scale crystallization should occur at mass deposition rates below those that would promote the uptake of this kind of impurity.

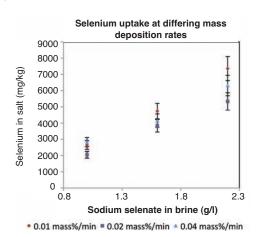


Figure 10—Uptake of selenium by sodium sulphate at differing mass deposition rates

Conclusions

The findings indicate quite conclusively that selenium is not present as a liquid inclusion. Due to the fact that chloride, which is the most concentrated non-crystallizing species present in the brine, is not a major contaminant, it can be concluded that liquid inclusion is not a significant contributor to the uptake of impurities in this system. It is predicted that isomorphous substitution, not liquid inclusion, will have the greatest impact on salt purity in the application of EFC.

It was determined that selenium was present in the form of selenate, and the similar structure and properties of selenate to sulphate allowed selenate to be isomorphously included in the sodium sulphate crystals. It is possible that selenium is present in the brine in other forms as well, but it is specifically the selenate form that manifests as an impurity. This serves to strengthen the theory that selenium is included as an isomorphous substitution.

In addition to the impact of excess sodium on the uptake of selenium, investigations were conducted to determine if the common ion between sodium chloride and sodium sulphate was the cause of the increased uptake of selenium, or the increased ionic strength of the solution. Here it was found that increasing ionic strength did not exhibit any impact on the impurity uptake. This, in addition to the fact that sodium chloride had a far greater impact on the uptake of selenium than potassium chloride, led to the conclusion that it was specifically the presence of the excess sodium ions that was promoting the uptake of the selenium impurity.

The impact of mass deposition rate on the uptake of selenium by sodium sulphate was investigated. It is believed that at higher mass deposition rates there is an increased probability that selenate is accidentally incorporated into the growing sodium sulphate crystals. Despite the experiments achieving consistent mass deposition rates, there did not appear to be a noticeable correlation between deposition rate and impurity uptake.

It is unlikely that the selenium impurity can be significantly decreased by process control variables, because the uptake was not greatly affected by mass deposition rates. The impurity uptake is facilitated by the similarity between selenate and selenite. To decrease the uptake of selenium, the concentration of selenate ions in the brine must be reduced before crystallization occurs.

It is believed that isomorphous substitution will have the greatest impact on product purity when applying EFC to most industrial brines. This is attributed to the small impact of liquid inclusion encountered in these experiments, and the large variety of dissolved components found in industrial brines. With many different dissolved species present, it is likely that an isomorphous relationship could occur.

This work represents the initial stages into the understanding of the predominant mechanisms by which impurities are taken up in an EFC application. Further investigation will be required, but it is hoped that this work will serve as a preliminary indicator of what direction the research should take.

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