Published online www.heatexchanger-fouling.com

MITIGATION OF SODIUM FLUORIDE SCALE IN AN EVAPORATOR-CRYSTALLIZER

R. Breault, G. Hamel and N.-A. Bouchard

Rio Tinto Alcan, Arvida Research and Development Centre 1955 Mellon Boulevard, P.O. Box 1250 Jonquière, QC, Canada G7S 4K8 <u>Raymond.breault@riotinto.com</u>

ABSTRACT

In April 2008, Rio Tinto Alcan inaugurated a new plant for the treatment of the spent potlining (SPL), a hazardous waste from the aluminum smelting operation. This plant, built in Québec (Canada), can process up to 80,000 tons of SPL per year using a new process, the low caustic leaching and liming process (LCL&L), developed at Rio Tinto Alcan's Arvida Research and Development Centre (Grolman et al. 1995, Hamel et al. 2009 and Kasireddy et al. 2003). The main operations of that process, after grinding of SPL, are: solubilization of all fluoride and cyanide bearing compounds in a caustic solution, separation of the insoluble carbon and the brick portion of the spent potlining, high temperature decomposition of the free cyanides and the ferro-cyanide, precipitation of the sodium fluoride in an evaporator-crystallizer and, finally, the conversion of the NaF to CaF2 by reacting NaF with lime $(Ca(OH)_2)$ in solution.

A critical step for scaling, in this process, is the NaF precipitation in the four-stage 150 m^3/h evaporatorcrystallizer, where the fluoride solubility decreases as the caustic concentration increases, leading to the NaF precipitation. Since the sodium fluoride concentration is supersaturated at all times during the evaporation process, scaling will occur.

In this paper, we describe the different types of scale encountered in different parts of the equipment and how scaling was minimized by modifying the operating parameters and by changing the internal caustic concentration profile within the four different evaporation effects.

INTRODUCTION

Growth scale and precipitation have a lot in common since, in both cases, their driving force is the solution supersaturation of a salt in solution. For an apparatus specifically designed to operate under supersaturated conditions such as an evaporating crystallizer, scaling is something that has to be dealt with on a daily basis since scale-free operations are not within reach for most processes operating under those conditions. However, there are operating conditions that will minimize scaling when some fundamental principles are applied. For example, a heat exchanger operating with a very low temperature gradient across the heat exchanger tube wall will minimize scaling at the expense of increasing the cost for the extra heat exchange surface area.

The spent potlining (SPL) is a mix of silica and alumina bricks used to insulate the steel shell and carbon blocks that serve as the cathode in the aluminum smelters' electrolytic cells. After four to five years of operation, the cell lining has to be rebuilt. Since the electrolytic bath used to dissolve the alumina is melted cryolite (Na₃AlF₆), some of it will be present with SPL along with NaF, cyanides and aluminum. The spent potlining will react with water generating flammable gases, mostly H₂, CH₄ and ammonia, and is classified as a hazardous waste because of water soluble fluorides and cyanide compounds. Without going into all the details of the LCL&L (Low Caustic Leaching and Liming) process for the treatment of the spent potlining of an aluminum electrolytic cell, the process was designed to separate the main constituents for recycling. Amongst these constituents are the fluoride compounds present in SPL that can be extracted using a caustic solution (NaOH) at low concentration. In contact with a low caustic solution, cryolite and aluminum will be dissolved according to the following reactions:

 $Na_{3}AlF_{6} + 4NaOH \rightarrow 7Na^{+} + Al(OH)_{4}^{-1} + 6F^{-}$ (1)

$$Al + NaOH + 3H_2O \rightarrow 3/2H_2 + Al(OH)_4 + Na^+$$
(2)

In accordance with the common ions effect on the solubility-product of NaF, the solubility of fluorides will be affected by all dissolved sodium salts. However, the dissolution of metallic aluminum should not really have any effect on the fluoride solubility since the sodium ions are still in solution.

In the particular case of the spent potlining treatment, the total sodium (TS) in solution would be:

$$TS = \sum Na^{+} = Na^{+}_{NaOH} + Na^{+}_{Na2CO3} + Na^{+}_{NaAL(OH)4}$$
(3)

The following figure shows the fluoride solubility as a function of the total sodium (TS) obtained from the experimental data compiled in Table 1.



Figure 1. Fluoride solubility as a function of total sodium at ambient temperature (22°C).

Table 1. Fluoride solubility for various sodium and aluminate concentrations ($T = 22^{\circ}C$).

TS	NaOH	Na ₂ CO ₃ NaAl(OH) ₄		F
g/L	g/L	g/L	g/L g/L	
0.6	0	1.4	0	19
1.1	0.4	3.2	0	18.9
1.4	0	3.2	0	18.2
14.3	21.5	4.4	0	13.8
18.1	29	3.4	0	12.9
22.7	37	3.4	0	11.6
6.7	5	4.4	9.9	16.6
7.7	10	4.4	0.2	16.2
11.8	11.9	3	18.8	14
12.8	11.6	4.4	21.7	14.1
23.1	25.2	2.6	38.5	11.2
23.7	24	3.4	42.9	11.7
35.8	38.5	5.9	57	8.5
36.4	36.7	6.2	65	8.5
47	51.7	5.6	76.5	6.4
47.7	49.3	6.8	84.6	6.7
6.5	4.1	1.4	18.4	16.5
12.1	8.8	6.5	22	13.4
23.8	18.7	16.1	30.9	9.6
36.3	28.5	23.5	50.1	7.5
48.3	37.8	31.7	65.9	5.9
76.3	61.7	7.2	193.6	4.8
93.9	75.3	9.3	239.4	3.5
122	98.3	10.5	315	2.1
168.8	134.8	20.5	421.9	1

This table presented the soluble fluoride for different caustic, carbonate and aluminate concentrations.

The following equation expresses the fluoride solubility as a function of TS, which is dependent on the three aforementioned parameters.

$$[F] = 4.47 + 14.8e^{-0.031775} - 0.0206TS$$
(4)

Since the fluoride ion solubility decreases with the increase of the caustic concentration, sodium fluoride precipitates when the solution is evaporated. In Figure 2, we have a representation of the evaporator-crystallizer as used at Rio Tinto Alcan's spent pollining treatment plant.



Figure 2. Schematic of a four-effect evaporating-crystallizer as the one used at Rio Tinto Alcan's spent potlining treatment plant.

In the following table, we have some of the design data for each effect and the characteristics for the four two-pass heat exchangers (Table 2).

Table 2. Nominal design conditions for the evaporatorcrystallizer

		Feed tank	First effect	Second effect	Third effect	Fourth effect
Liquor exiting	m ³ /h	150	102	80	48	17
Temperature	°C	90	101	91	75	65
TS	g/l	22	33	42	72	203
[F]	g/L	9	12.8	11	5.9	0.6
Solids	%	0	0.1	1.2	4.3	16
Evaporation	MT/h	N/A	49	20	31	31

Basically, this unit will evaporate a caustic solution that is fed at a flow rate of 150 m³/h, 50 g/L NaOH and 10 g/L F to 340 g/L NaOH and 1 g/L F, generating a NaF precipitate that is filtered, leaving a concentrated caustic solution. Since the fluoride content in the spent potlining will depend on the smelter technology and the pot dismantling practice, the spent potlining feed rate will be varied to maintain the fluoride content in the digest solution at a target value set at 10 g/L.

In the original design of the evaporating-crystallizer, part of the concentrated solution of the fourth effect containing some NaF crystals was returned to the second effect to provide seed material. No NaF was precipitated in the first effect of evaporation since the saturation was not reached Very early after the plant start-up, heavy scaling of the unit was experienced. Scale formed on the tube sheet at the exit of the first effect heat exchanger tubes and scale was also forming on the side wall of the evaporating tank below and above the solution level. All these three types of scale, when detaching from their support, would immediately block the liquor flow through the heat exchanger, causing a plant shut-down. Even if all three types of scale had a similar consequence, that is a plant shut-down, their fundamental cause was very different.

Examples of the first effect heat exchanger tube sheet scaling are shown in Figures 3 and 4. The scaling of the third effect heat exchanger tube blockage is shown in Figure 5.



Figure 3. First effect scaled two-pass heat exchanger. Lower section is the exit and the top section is the return.



Figure 4. Close-up of the tube sheet scaling of the first effect heat exchanger.



Figure 5. Tube inlet blocked by crushed scale on the third effect two-pass heat exchanger. No scale seen at the exit of the tubes (bottom section).

Due to the relative importance of this scaling issue and the heavy impact on the plant operations, the plant management decided to address this in a global way, using the Business Improvement and Lean-Six sigma tools. These are part of Rio Tinto Alcan's way to operate and allow to measure, address and improve all aspects, from equipment design to operating procedures and good practices.

FUNDAMENTAL CAUSES AND SOLUTIONS FOR THE DIFFERENT TYPES OF SCALE

Scaling of the evaporating tank above the liquor level

Scaling of the side wall above the liquor level is related to splashing of the liquor and to entrained liquor droplets. This can be minimized by a more stable operating control of the liquor level to ensure that the liquor return line is submerged at all times. Prevention of vacuum fluctuation due to rapid temperature changes is also very important. These fluctuations could lead to sudden liquor boiling and increase of the droplet entrainment. However, even by a very tight control of the operation, the scale formation above the liquor level cannot be totally eliminated and it will most likely continue to be present. Thus, avoiding any thermal shock is also important to prevent scale from detaching. One solution to prevent the detached scale from being crushed by the recirculation pump and blocking the entry of the exchanger tubes was to add a mesh basket so that any detached scale large enough to block the tubes would be retained inside the evaporating tank and accumulated at the bottom (Figure 6).



Figure 6. Mesh basket (1.5-inch mesh) inserted in the return pipe entrance before the circulation pump to prevent tube entrance blockages by detached scale.

Scaling of the evaporating tank below the liquor level

The LCL&L process for the treatment of spent potlining is composed of several steps: crushing, leaching, high temperature cyanide destruction, liming with solid liquid separation by filters and decanters in addition to the evaporating-crystallization. Whenever some operational problems were encountered elsewhere in the process, the vapour on the evaporator-crystallizer was shut-down and each effect was put on recirculation. However, very often when the steam was put back-on, a sudden overload of the amperage of the recirculation pump would then be observed, causing a total shut-down of the unit.

This phenomenon can be explained by the Ostwald ripening. The mechanism by which large crystals are formed by dissolution and reprecipitation of small crystals was first described by Ostwald in 1896. This particular phenomenon is generally observed when solids with a large size distribution are maintained in contact with the saturated solution for a certain period of time. Since small particles have a much higher surface energy than large particles, they will dissolve and reprecipitate on larger particles, tending towards a mono-size particle distribution, thus minimizing the total energy. In the case where the precipitate can adhere to the wall of the vessel, scaling will then also be enhanced under those conditions.

The following figure shows the NaF particle size distribution, before and after the steam was shut off and the effect maintained on recirculation. It can be observed that all particles smaller than 15 microns have disappeared (Figure 7).

Demonstrating a correlation between this tendency towards a mono-size particle size distribution and scaling of the evaporating vessel wall below the liquor level is not obvious. However, every time the plant had to stop the steam for a long period (day), the plant had to stop the evaporator-crystallizer every time the steam was reintroduced to the heat exchanger. There was a sudden increase of the liquor circulating pump amperage, forcing a complete stop of the operation. After opening the head of the heat exchanger, it could be observed that the entry of the tubes was blocked with scale platelets as shown in Figure 5.



Figure 7. NaF size distribution before, and three days, after stopping the steam.

A thick dense scale is generally observed under low supersaturated conditions such as those encountered when an evaporating effect is maintained under circulation, with no steam and no addition of fluoride ions. To avoid these particular conditions, the evaporating circuit was modified such that when the spent potlining digestion had to be stopped, the fluoride feed to the evaporator-crystallizer was maintained by dissolving the NaF crystals in a low caustic solution, and this solution fed back at the first effect. Doing so, the evaporating-crystallizer could be maintained under steady state conditions with the steam injection, even if the other operations of the plant were stopped. Of course, steam is wasted, which increases the operating costs and it can only be maintained for a short period of time, but ever since this procedure was implemented at the plant (mid 2010), no blockage caused by scale platelets was experienced.

Scaling of the first effect's tube sheet

Scaling of the heat exchanger tube sheet when the liquor exits the tubes is quite a unique phenomenon since, most of the time, scaling will occur inside the tubes. Nevertheless, this type of scaling was also responsible for unscheduled shut-downs of the evaporator-crystallizer since, as can be seen in Figure 1, when the chunks of scale detached from the tube sheet, they blocked the second pass, thus stopping the liquor flow. To be able to explain this unique phenomenon, we have to look at the fluoride ion concentration and the caustic concentration inside each effect of the evaporator-crystallizer. In the following graph (Figure 8), the total sodium in the feed and for each effect is shown for three different operating modes of the evaporator-crystallizer:

1) no recirculation of concentrated liquor from the fourth effect;

2) with recirculation of concentrated liquor to the second effect and;

3) with recirculation of concentrated liquor to the first effect.

The dotted line shows the expected total soda concentration due to the water evaporation for each effect.



Figure 8. Total sodium concentration through the evaporator-crystallizer without recirculation (measured and estimated), with recirculation at the second effect and with concentrated liquor recirculation at the first effect.

On this graph, we can see that the measured and expected total sodium concentrations are very similar throughout the four effects when there is no recirculation. When some concentrated liquor is returned to the first effect, we can see that the total sodium concentration is significantly higher than without recirculation. The same increase is observed when concentrated liquor is returned to the first effect. Of course, the recirculation of concentrated liquor has no effect on the steam consumption; it only modifies the total sodium concentration profile within the evaporator-crystallizer and, therefore, plays on NaF precipitation pattern in the four effects.

In Figure 9, we have the fluoride ion concentrations for the same conditions as for Figure 8.



Figure 9. Expected and measured fluoride ion concentrations through the evaporator-crystallizer, with and without recirculation at the first effect.

In Figure 9 we can see that when there is no return of concentrated liquor to the first effect, even if the fluoride concentration increases from 8 g/L in the feed to 14 g/L in the first effect vessel, which is slightly above the equilibrium concentration determined from Eq. 1, it is not enough to generate NaF crystals. However, this slight NaF supersaturation is enough to generate the scale formation at the exit of the tubes. At the exit of the tubes, there will be a pressure drop and an increase of the turbulence, which could be responsible for the nucleation of NaF and its adherence to the tube sheet.

To solve this problem, the concentrated liquor return line was changed from the second effect to the first effect of the evaporator-crystallizer. This change had two very important impacts. The most important impact was that by increasing the total sodium ion concentration, the NaF solubility was significantly decreased in the first effect vessel, leading to NaF precipitation. Secondly, since there are NaF crystals returned with the concentrated liquor, they also provide NaF seeds. These two changes have completely prevented the tube sheet scaling from occurring again and therefore, prevented unscheduled plant shut-downs.

Figure 9 also shows that for all four effects, the fluoride concentration always exceeds the equilibrium concentration. This would indicate that some scaling could continue throughout the evaporator-crystallizer. However, with the return of NaF seeds and concentrated liquor at the first effect, the supersaturation is also reduced.

CONCLUSIONS

The four-effect evaporator-crystallizer scaling and blockages were some of the major roadblocks on the rampup of the first-of-its-kind LCL&L process based plant. This had to be addressed in a global way, using all the relevant business improvement tools. Even if each situation dealing with scaling of an apparatus has to be studied case by case, there is a general rule that can help to minimize the extent of scaling. When facing crystallization scaling, avoiding metastable conditions certainly comes high on the list. This can be achieved either by diluting the supersaturated salt or, by doing the opposite, by increasing the supersaturation to enhance nucleation and crystal precipitation. This last approach was applied in two of our cases since the purpose of the evaporation is precisely to precipitate NaF. However, this approach is not applicable to the scale on the wall of the evaporating vessel above the liquor level. Here, a combination of best practices for the operation and a mechanical approach was the key to maintaining continuous operation, even if it did not address the fundamental cause of scaling.

ACKNOWLEDGEMENTS

The authors would like to give credit to all the spent potlining treatment plant personnel for their valuable input and willingness to make changes and to do things differently. Without them, none of this would have been possible.

REFERENCES

Grolman, R.J., Holywell, G.C., Kimmerle, F.M. and Turcotte, G.R., 1995, US patent 5,470,559.

Hamel, G., Breault, R., Charest, G., Poirier, S., and Boutin, B., 2009, From the "Low Caustic Leaching and Liming" Process Development to the Jonquiere Spent Potlining Treatment Pilot Plant Start-Up. 5 Years of Process Up-Scaling, Engineering and Commissioning, ed. G. Bearne, TMS (The Minerals, Metal & Materials Society), pp. 921-925.

Kasireddy, V., Bernier, J.-L. and Kimmerle, F.M., 2003, US patent 6,596,252 B2.