

THE CONTROL OF FLUORIDE CONCENTRATION IN ETİ ALÜMİNYUM BAYER REFINERY LIQUOR

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Abstract

In the ETİ Alüminyum Bayer Process liquors, fluoride is evident as an undesirable impurity, because it presents itself as a precipitate of Sodium Fluoride (NaF) in the higher concentration liquors, which has two mal effects, one of which limits the caustic concentration that ETİ can attain, and the other is its solid phase presents as scale.

Spent liquor from precipitation is fed to evaporators. To improve alumina extraction in autoclave liquor it was decided that the strong liquor caustic concentration be gradually increased. It was noticed that scale formation in the strong liquor pumps and pipelines dramatically increased. XRF and XRD characterized the scale as 'Villiaumite' (NaF). Research on Villiaumite found that it started to precipitate at higher caustic concentrations. The solubility of NaF was evaluated and saturation levels were determined. As a result of this study control of NaF precipitation is practiced by ETİ.

Introduction

Impurities in Bayer process liquors have an impact on product quality, liquor productivity, change of physicochemical properties of the liquor, and can form hard or soft scale on equipment, such as heat transfer surface, vessel walls, shafts etc. and pipes and valves. Bauxite is the source of the impurities since it is the main raw material. Impurities generally build up in liquor if not controlled.

ETİ started to see the impact of one of these impurities when we wanted to increase production capacity. With the start of capacity increase studies one initiative was to increase strong liquor caustic concentration in evaporator discharge thus enabling an increase in alumina dissolution in digestion. After starting to increase the strong liquor caustic concentration gradually, it was seen that at the routine sample point for evaporator product was cloudy. Research was done on the solids after filtering and drying by XRD (X-Ray Diffraction) and XRF (X-Ray Fluorescence) analyses. From these analyses, the precipitate was identified as 'Villiaumite'. This indicated that the F (fluoride) impurity in the liquor was precipitating out as Sodium Fluoride (NaF). This precipitate presented itself in strong liquor tanks, on pipelines and on pumps. This initiated further studies on methods of control of the fluoride.

Laboratory Test Works

To find a starting point for the laboratory work, process data was used to understand the behavior of the fluoride in liquor. ETİ's practice has been to analyze liquor impurities on a weekly basis for all Bayer liquors and Figure 1 shows fluoride concentration in strong liquor vs. caustic concentration. The graph clearly shows that fluoride solubility is decreasing with increasing caustic

concentration, strongly indicating that as the caustic concentration increased fluoride showed up as a precipitate of NaF. This preliminary test work led to the realization that a solubility curve of fluoride in caustic was needed. Laboratory works include solubility curve generation of NaF in varying caustic concentrations, temperature effect on NaF precipitation and also evaporative effect on spent liquor.

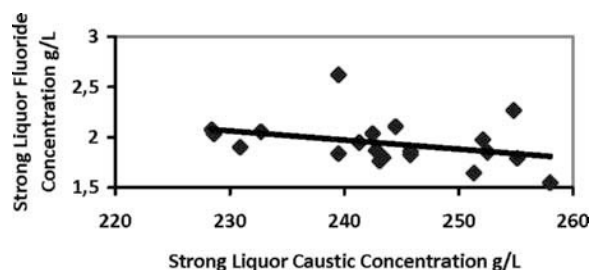


Figure 1. Relationship between fluoride and caustic concentrations in the strong liquor

Method of Obtaining Solubility Curve

The solubility curve was generated by using synthetic liquor and analytical grade NaF. Synthetic liquor concentration was adjusted as in the system and the starting concentration was 230g/l Na₂Oc as was the current situation at that time (Na₂Oc means NaOH as Na₂O, not total caustic without Na₂CO₃). The synthetic solution was put in a beaker at 86 °C with magnetic stirrer and stirring bar. Analytical grade NaF salt was added slowly till the first evidence of undissolved solids occurred and this was determined to be the equilibrium point. The same procedure was used for 4 different caustic concentrations and a solubility curve of NaF in caustic was formulated as shown in Figure 2.

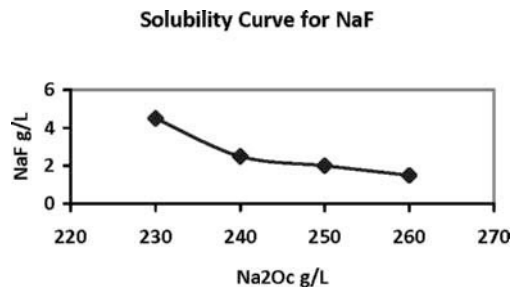


Figure 2. Solubility curve of NaF in synthetic caustic solution

Evaluating the Effect of Temperature

To examine the temperature effect on the solubility of the NaF in strong liquor, experiments were conducted at 90, 80 and 70 °C in a water bath and the procedure as described below was applied to each differential temperatures.

First of all, 1 l of strong liquor was taken from the process and granular NaOH was added to reach different caustic concentrations by the use of stirrer. Then, the samples with different caustic concentration were put in a 90°C water bath and kept for 15 hours, even though precipitation occurred in the first hour (Figure 3). The samples were then vacuum-filtered and washed with technical ethyl alcohol and oven dried at 105°C; following which the dried solid were subjected to XRF and XRD characterization.

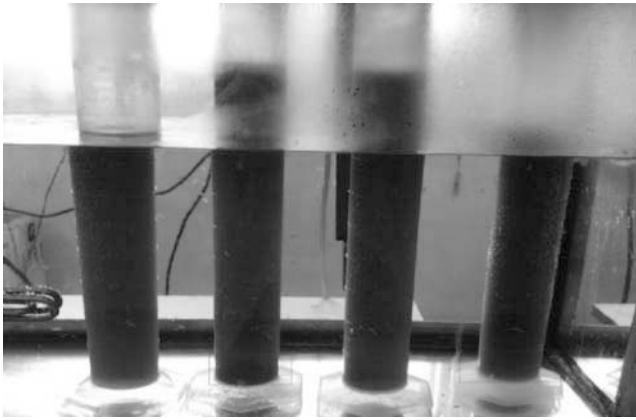


Figure 3. Solutions at different caustic concentrations in water bath

Results of the tests at 3 different temperatures are shown in the tables below. The tables clearly show for similar caustic concentrations at differing temperatures resulting in a relationship of increasing precipitation with decreasing temperature.

Table 1. Results of the solutions in 90 °C water bath

Sample No	Temperature (°C)	Caustic Concentration Na ₂ Oc(g/L)	Solid (precipitated) (g/L)
1	90	236	0
2	90	313	-
3	90	332	2,00
4	90	352	3,16

Table 2. Results of the solutions in 80 °C water bath

Sample No	Temperature (°C)	Caustic Concentration Na ₂ Oc(g/L)	Solid (precipitated) (g/L)
1	80	246	0
2	80	300	4,00
3	80	332	4,11

Table 3. Results of the solutions in 70 °C water bath

Sample No	Temperature (°C)	Caustic Concentration Na ₂ Oc(g/L)	Solid (precipitated) (g/L)
1	70	240	1,5
2	70	300	5,1
3	70	313	5,2

Furthermore, with the analyses of the precipitate using the XRD technique demonstrated that the solids were NaF. XRD characterizations are shown in the figures below for 90 °C and 70 °C. In Figures 4 and 5 the pattern of Villiaumite are clearly identified.

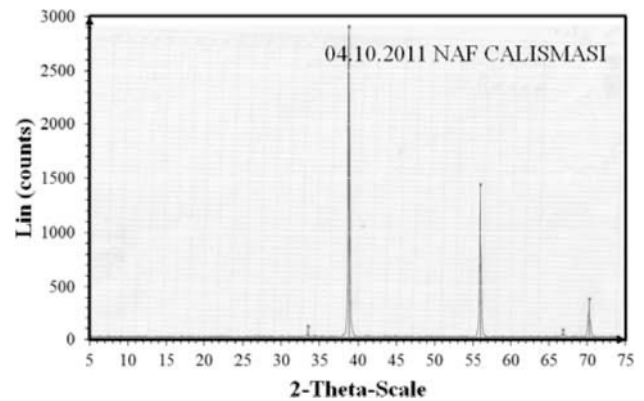


Figure 4. XRD characterization of 90 °C trial precipitate

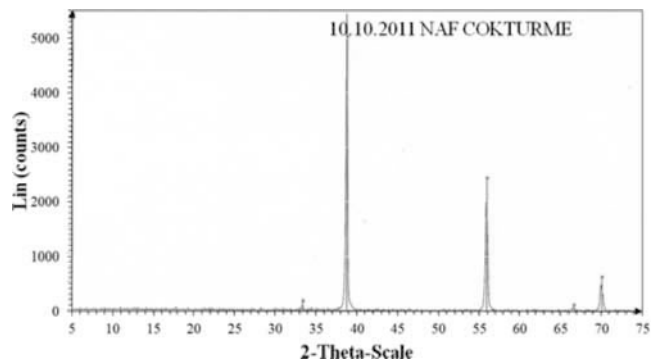


Figure 5. XRD characterization of 70 °C trial precipitate

Study on the effect of evaporation

ETİ has a 5-effect evaporation unit, to which spent liquor enters at nearly 135 g/l Na₂Oc and leaves as strong liquor at between 220 – 260 g/l Na₂Oc. A rotary evaporator was used for the study (Figure 6). Spent liquor was taken from the process and analyzed as 136 g/l Na₂Oc caustic concentration and was subjected to evaporation for 20, 30, 40 and 50 minutes. At each time interval liquor phase was analyzed by using Metrohm titrator, as well as the turbidity and precipitated solids was measured. Table 4 below shows the

alumina (Al_2O_3), Na_2O_c concentrations, the turbidity of the liquor phase analyses and also shows the solids precipitated (g/l). Figure 7 shows the relationship between Na_2O_c concentration and precipitated solids also is an indicator of what is going in the evaporator batteries.



Figure 6. Laboratory scale rotary evaporator

Table 4. Results of evaporative effect

Sample No	Time(min)	Al_2O_3 (g/L)	Na_2O_c (g/L)	Turbidity (NTU)	Solids (g/L)
1	0	59	136	5,0	0
2	20	91	210	22,0	0,67
3	30	93	217	27,0	0,97
4	40	123	284	58,0	2,3
5	50	133	303	112,0	2,9

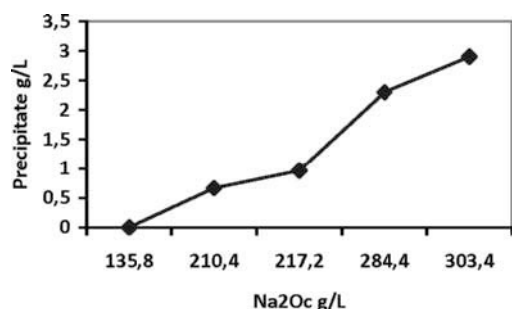


Figure 7. Effect of evaporation on solids and caustic concentration

Plant Trial

The previously described laboratory work provided information about the behavior of fluoride within the process. The precipitated NaF needed to be disposed of from the liquor; because it was evidencing itself as wall scale in the piping and the pumps. It was established that a salting out process as a side stream and using

thickeners for settling out the salt, was the most effective way that ETI had to easily handle the problem. A flow sheet for the side stream salting out process was generated and existing equipments were used for this process.

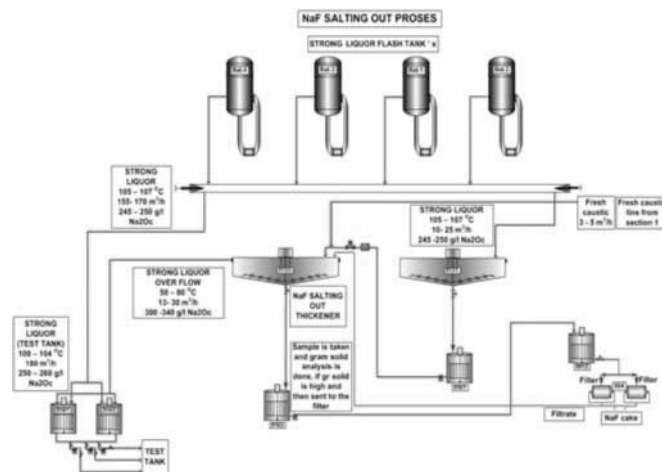


Figure 8. Process flow for NaF salting-out process

The process flow diagram is shown above clearly demonstrates how NaF was precipitated and settled. As mentioned in the laboratory work the high caustic concentration was used to precipitate NaF. Strong liquor was taken as side stream to the thickeners, two in series, and fresh caustic was added to the second stage of thickening. Underflow of the second thickener was collected in an underflow tank and then filtered through a drum filter depended on the solid content in the underflow. The overflow was sent to Test Tanks and blended with the main strong liquor flow at the Test Tank. Feedback control was used for the process, because the Test Tank caustic concentration was considered as being important for the start of the Bayer process. The flow of the side stream and the fresh caustic addition was controlled according to the requirements of the Test Tank liquor caustic concentration. Furthermore the concentration of the second thickener was controlled to ensure optimum precipitation of the NaF. The underflow was filtered by using a 1m wide drum filter (see Figure 9 below).



Figure 9. Filtration of thickener underflow

Post-Filtration Cake Treatment

The cake residue from the above plant trial was discharged from the filter and collected in stainless steel pan, after which the cake was dried in an induction furnace at 200°C until it tested moisture free. In the Figure 10 below you can see the wet cake on the left hand side and the dried cake on the right hand side.

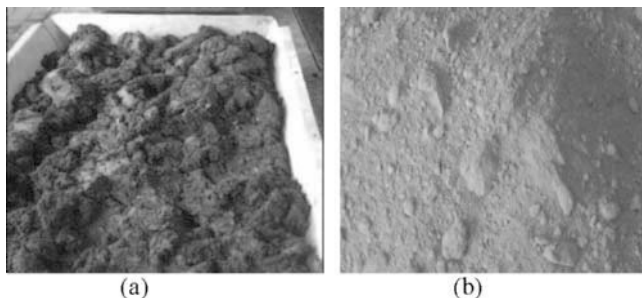


Figure 10. (a) Wet cake of NaF before drying (b) Dried cake of NaF

The Table 5 and the XRD Figure 11 below other results of analysis of the dried cake. The last Figure 12 below is a picture of the resultant packaging of the dried cake for storage.

Table 5. Chemical and Physical analysis results of dried NaF at 200°C

		Chemical Analyses (XRF %)										
The NaF cake dried at 200°C	Moisture	Na	F	Al	K	Si	Ca	S	Fe	V	Cl	Ga
	0,54	57,5	38,8	2,51	0,71	0,1	0,18	0,018	0,063	0,058	0,015	0,0072
	Physical Analyses											
d 50	+149 μ	-149 +74 μ	-74 +44 μ	-44 +20 μ	-20 μ	+44 μ						
	18,48	2,06	7,46	11,12	25,46	53,9	79,36					
Purity of NaF %	86											

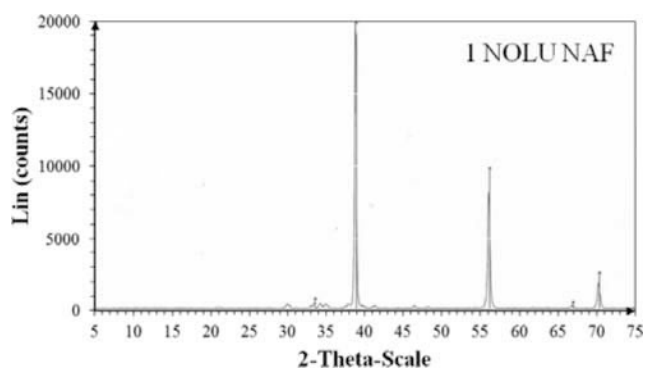


Figure 11. XRD pattern of filtrated and dried NaF



Figure 12. Packed NaF

Ongoing Test Work

It is recognized that there is a under current operating conditions a limit to how high the evaporator discharge caustic concentration can be driven. As a result of this test work is currently being carried out in the laboratory using the banch scale rotary evaporator as per the initial test work.

Conclusion

In conclusion, ETI and Hatch identified the root cause of an issue that was creating a problem in the discharge of the evaporators wherein excessive and process inhibiting scale was being formed in the discharge equipment. The test work that was conducted by ETI, in response to the above led to the understanding of the main cause, which is the NaF precipitation at ETI's evaporator product, as the plant caustic concentration was increased. Consequently, this understanding has allowed ETI and Hatch to develop a fluoride removal process, which has reduced NaF scale formation on the evaporator product and Test Tank lines and so has allowed ETI to actually increase the caustic concentration to above previous limits. Research is continuing to enable ETI to work with even higher caustic concentrations.

References

There were no related refences found in literature, all research, laboratory tests and plant trial were done in house by ETI.