Test of Powdery Bedding Materials for Use Underneath Cathode Blocks

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Abstract

Different bedding materials have been considered for use in aluminum electrolysis cells. A bedding material is the substance placed just below the cathode blocks, often serving as a leveling agent. However, the barrier properties of these materials have not always been thoroughly considered. In this study, we describe the development of a lab-scale test designed to evaluate various bedding materials with respect to their barrier properties. We have theoretically evaluated different powders and discussed their performance in the chemical tests conducted. This comprehensive approach aims to provide a deeper understanding of the suitability of different bedding materials in enhancing the efficiency and longevity of aluminum electrolysis cells

Keywords: Aluminium electrolysis, Lining materials, Powdery bedding materials.

1. Introduction

Today, alumina intended for electrolysis is used as bedding material underneath the cathode blocks. The bedding material is typically 20–40 mm thick and constitutes a significant part of the bottom lining. Different bedding materials have been utilized in Hydro. Initially chamotte powder and ramming paste was used in many plants, but the use was stopped due to unknown reason, and typically replaced by smelter grade alumina. The advantage of alumina is its availability in the plants and simplicity of the installation. However, smelter grade alumina has not the desired barrier properties, and a test program was carried out to evaluate different bedding materials with respect to their barrier properties.

A secondary objective with this work was to test AlF_3 as barrier material, an idea since it normally basic bath that is found underneath the cathode block in a cell after shut-down. The basic bath rich in NaF should then react with AlF_3 to form solid cryolite and thus form a solid material according to reaction (1).

$$NaF\ (l,\ bath) + AlF_3(s) \text{ --> } Na_3AlF_6(s) \qquad (1)$$

2. Experimental

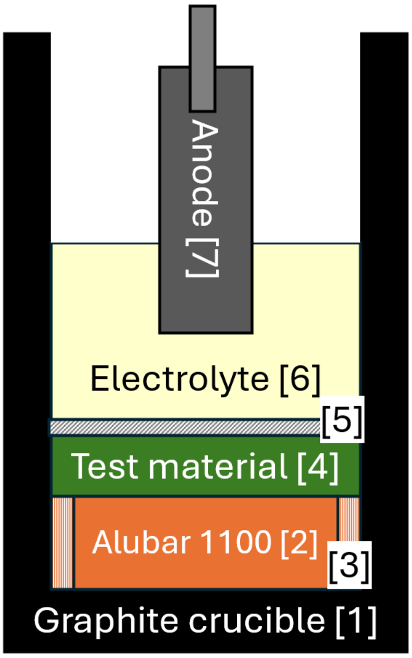
2.1 Polarized Chemical Exposure

To simulate the conditions in an electrolysis cell and at the same time achieve reasonable reaction of the bedding material, a new test set-up was designed. The test set-up is shown in Figure 1 (left) and comprises of:

1) A graphite crucible which is also the working cathode in the experiment
2) A reference barrier brick (Alubar 1100) placed in the bottom of 1) of height 30 mm and diameter 100 mm
3) Crushed barrier brick (Alubar 1100) (< 1.18 mm) to fill the small gap between 1) and 2)
4) 20 mm of compacted test bedding material placed on top of 2) and 3)

5) A thin plate (~5 mm) of cathode block grade (N-4 from Energoprom) acting as a membrane. The plate was glued to the crucible with a carbon glue (AD20, Tokai COBEX)
6) 800 g of electrolyte: cryolite (CR = 3.4), 10 % Al_2O_3.
7) Anode (Ø30 mm) with a steel connection. The anode material was a graphitized cathode block carbon.

The tests were run at 970 °C with 10 A current for a duration of 25 hours.



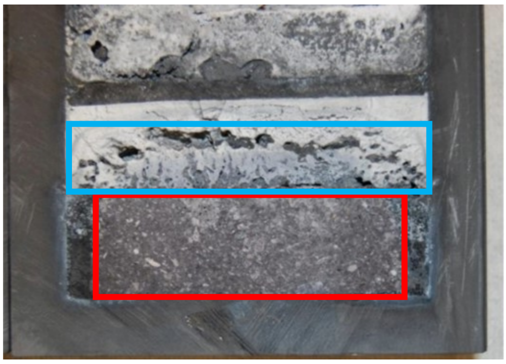


Figure 1. Left: Sketch of test set-up, Right: Example of cross-section after test. Blue frame indicates original bedding material. Red frame indicates original barrier brick, and the height of the red frame after the test is compared with the initial height of the brick.

The tests are listed 1–12 in chronological order. After the tests, the crucibles were cut in two parts with a diamond saw. The extent of reaction in the bedding material was assessed visually, an example is shown in Figure 1 (right). The height to unreacted (visually assessed) material of the Alubar 1100 reference brick was measured with a caliper.

The current and voltage were recorded for each experiment. There was some short-circuiting during the tests, and the electrolysis time varied from 16 to 24 hours.

2.2 Materials

The materials used in the tests are given in Table 1. The composition is taken from the supplier specification. The spent refractory brick was not analyzed but consisted of glassy lens material of black color.

Table 1: Bedding materials used in the tests.

Material	Specification/producer	Composition [wt%]	Test
AlF_3	Boliden, smelter grade	> 95 % AlF_3	1, 2, 5, 9
Alumina	Smelter grade	> 99 % Al_2O_3	3, 11
Crushed Alubar	Alubar 1100 from Simonsen. Crushed and sieved < 1.18 mm	68 % SiO_2 26 % Al_2O_3 < 3 % Fe_2O_3	4, 12
Spent refractory brick	Alubar 1100 from Simonsen. Sample from a cell of 2053 days, Crushed and sieved < 0.15 mm	NA	6
Ramming paste	S20EF, Carbon Savoie	C + volatiles	7
Ramming paste	Elseal T ,Elkem	C + volatiles	9
Clayburn Dri-Barrier Mix (DBM)	Dri-Barrier Mix, India source	53-59 % SiO_2 21-27 % Al_2O_3 1-3 % Fe_2O_3	8
Olibar	Powder, Sibelco	42 % MgO 44 % SiO_2 7 % Fe_2O_3 4 % Al_2O_3	10

3. Test Results

3.1 Test 1: AlF_3

In test 1, smelter grade AlF_3 was tested, and the result is shown in Figure 2. The membrane plate 5) loosened, and the test was redone. The loosening of the membrane led to direct contact of electrolyte and the bedding material and thus an excessive reaction.

Figure 2. Cross-section of crucible after Test 1 with AlF_3 as bedding material.

3.2 Test 2: AlF_3

In test 2 smelter grade AlF_3 was redone, and the result is shown in Figure 3. The bedding material AlF_3 is fully reacted/infiltrated. The barrier brick is heavily reacted in the upper part, but slightly less than in test 1.

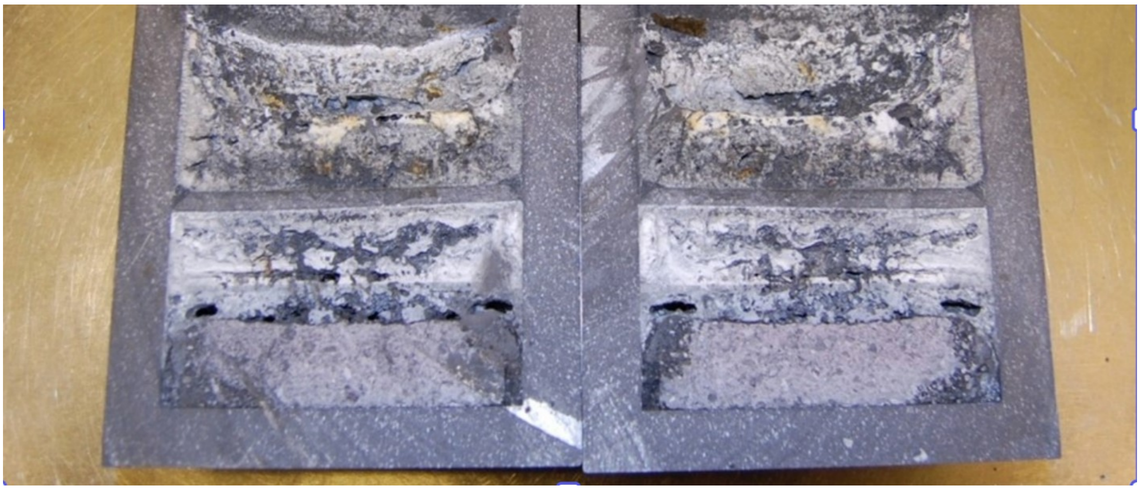


Figure 3. Cross-section of crucible after Test 2 with AlF_3 as bedding material.

3.3 Test 3: Alumina

In test 3, smelter grade alumina was tested, and the result is shown in Figure 4. The bedding material Al_2O_3 is fully reacted/infiltrated, and the barrier brick is reacted in the upper part. A part of the anode fell off and is seen the electrolyte.

Figure 4. Cross-section of crucible after Test 3 with Al_2O_3 as bedding material.

3.4 Test 4: Crushed Alubar 1100

In test 4, crushed Alubar was tested, and the result is shown in Figure 5. The barrier brick is intact, and the bedding material appears in two layers. Upper layer is reacted/infiltrated bedding powder and lower layer is still in powdery form.

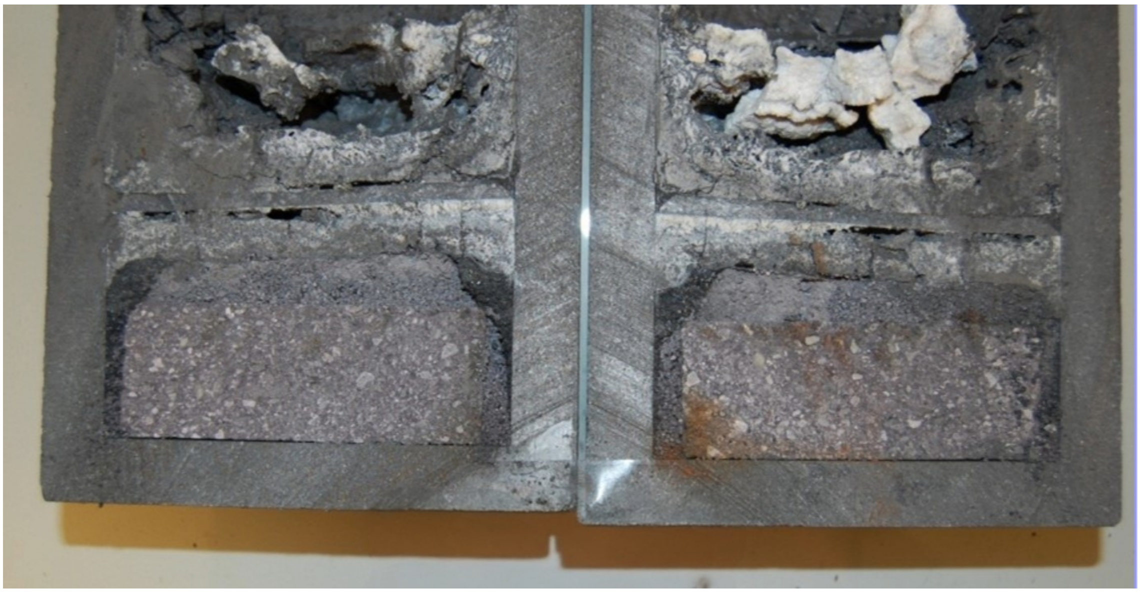


Figure 5. Cross-section of crucible after Test 4 with Alubar 1100 as bedding material.

3.5 Test 5: AlF_3, not Polarized

In test 5, the test set-up was different from the other tests in this paper. The barrier brick was just embedded in smelter grade AlF_3 and heated to 900°C for 3 hours, and the result is shown in Figure 6. The sample had clearly reacted with AlF_3, and white fume (SiF_4) was produced during the test. A 2–4 mm reaction zone around the sample was observed.

Figure 6. Cross-section of sample after Test 5, where Alubar 1100 was embedded in AlF_3 at 900 °C for 3 hours, without electrolysis.

3.6 Test 6: Spent Refractory Brick

In test 6, crushed spent refractory brick (Chamotte based) was tested, and the result is shown in Figure 7. The barrier brick is slightly reacted in the upper part. The barrier material had consolidated to a dense product.

Figure 7. Cross-section of crucible after Test 6 with spent refractory brick as bedding material.

3.7 Test 7: Ramming Paste

In test 7, ramming paste was tested, and the result is shown in Figure 8. The ramming paste was infiltrated with electrolyte and the barrier brick is discolored/reacted in the upper part. A part of the observed discoloration might be due to movement of the binder before baking of the ramming paste, but there is also signs of bath components in the reacted brick.

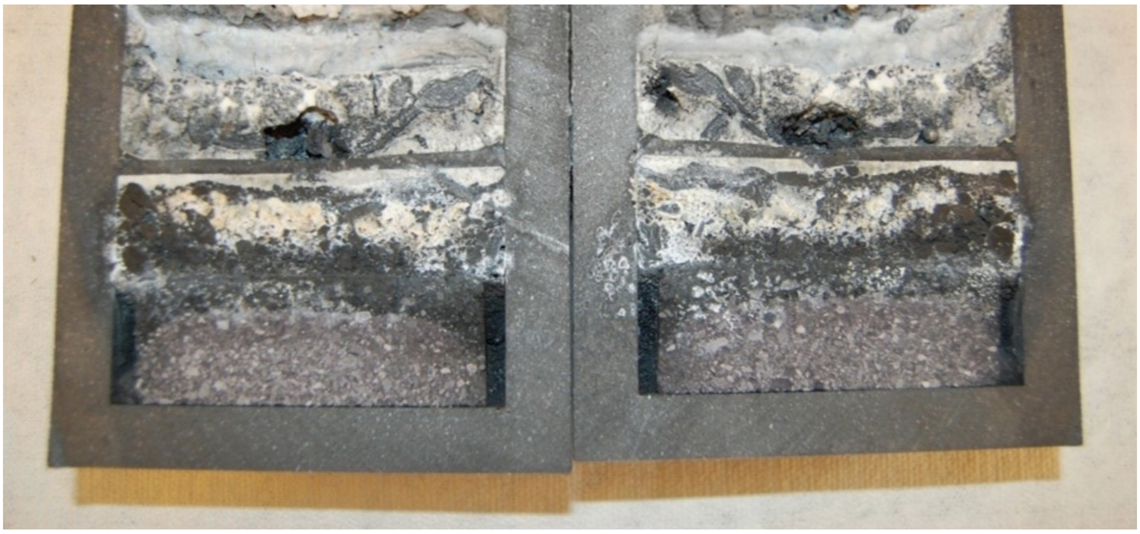


Figure 8. Cross-section of crucible after Test 7 with ramming paste as bedding material.

3.8 Test 8: Clayburn Dri-Barrier Mix

In test 8, Clayburn DBM was tested, and the result is shown in Figure 9. The barrier brick is intact, and the bedding is reacted only in the upper area. Underneath the reacted zone the powder is still loose.

Figure 9. Cross-section of crucible after Test 8 with Clayburn Dri-Barrier Mix as bedding material.

3.9 Test 9: AlF_3 and Ramming Paste

In test 9, ramming paste and AlF_3 were tested in two-layer bedding. Ramming paste was facing the refractory brick, and the purpose of the ramming paste was to avoid direct contact between AlF_3 and the refractory brick and thus to avoid SiF_4 formation. The result is shown in Figure 10. The refractory brick is slightly reacted in the top, and the ramming paste is fully infiltrated with electrolyte. As in Test 7, some of the discoloration of the refractory brick might be due to melting of the binder in the ramming paste before the ramming paste becomes baked.

Figure 10. Cross-section of crucible after Test 9 with AlF_3 and ramming paste as bedding material.

3.10 Test 10: Olibar

In test 10, Olibar (olivine powder) was tested, and the result is shown in Figure 11. The barrier brick is intact, but the bedding material is reacted/infiltrated.

Figure 11. Cross-section of crucible after Test 10 with Olibar as bedding material.

3.11 Test 11: Alumina, Second Run

To investigate the reproducibility of the test method, Test 3 with alumina was redone. The result after the test is shown in Figure 12. Comparison of Test 3 and Test 11 is shown in Figure 13, and the two tests are in good accordance.

Figure 12. Cross-section of crucible after Test 11 with Al_2O_3 as bedding material.

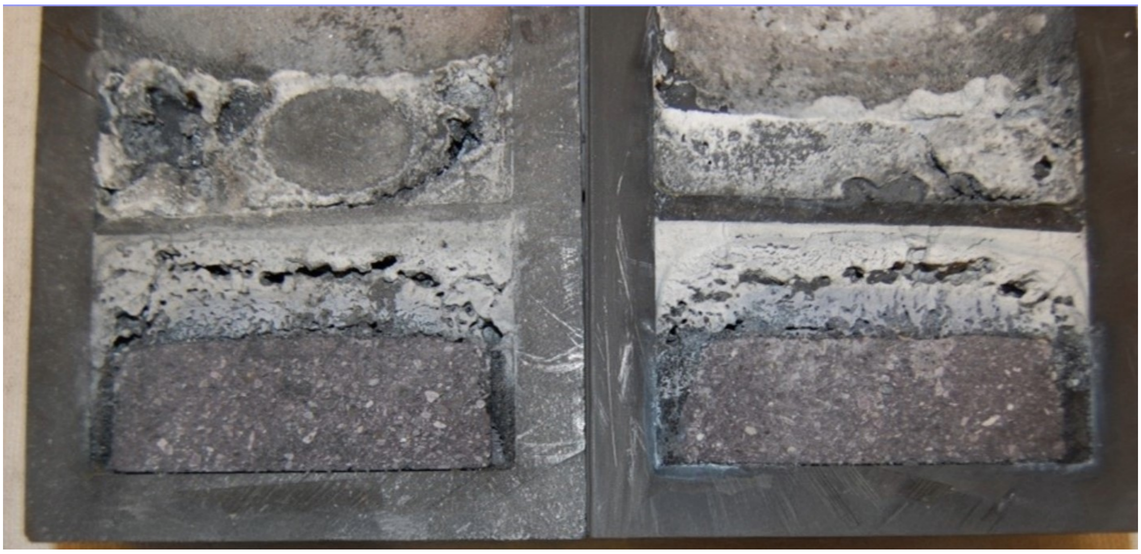


Figure 13. Comparison of parallel Test 3 (left) and Test 11 (right) with Al_2O_3 as bedding material.

3.12 Test 12: Crushed Alubar 1100, Second Run

To investigate further the reproducibility of the test method, Test 4 with crushed Alubar 1100 was redone. The result after the test is shown in Figure 14. The barrier brick is intact, and the barrier appears in two layers. Upper layer is reacted/infiltrated barrier powder and lower layer is powder. Comparison of Test 4 and Test 12 is shown in Figure 15, and the two tests are also in good accordance.

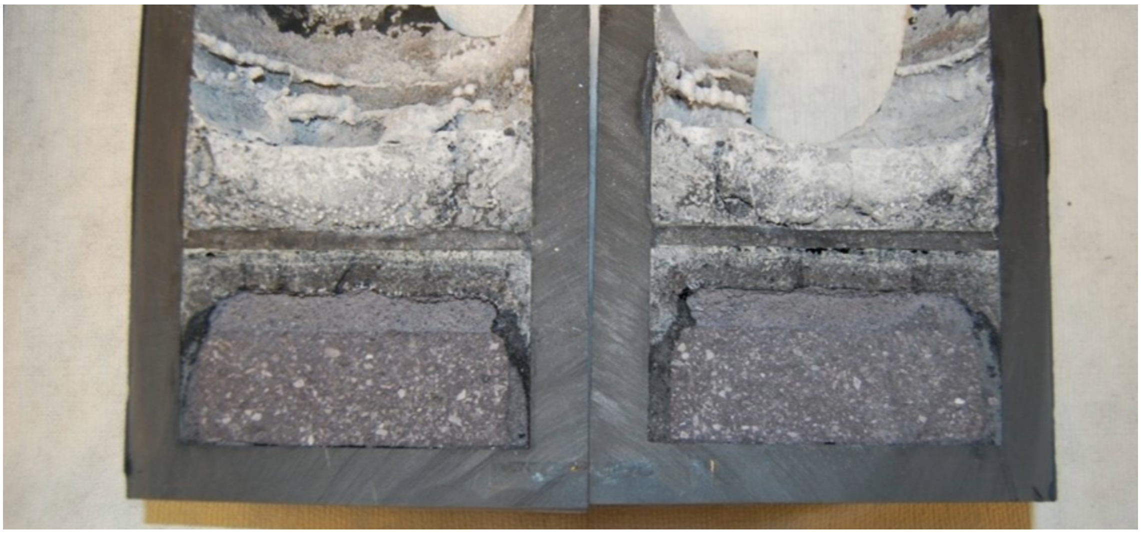


Figure 14. Cross-section of crucible after Test 12 Alubar 1100 as bedding material.

Figure 15. Comparison of parallel Test 4 (right) and Test 12 (left) Alubar 1100 as bedding material.

3.13 Summary Table of Test Results

The results are summarized in Table 2. There is a difference in the reaction depth in both the barrier brick and in the bedding material.

Table 2. Summary of tests 2–12.

Test No.	Barrier Material	Refractory Initial height [mm]	Refractory Unreacted height* [mm]	Refractory Reacted height [%]	Reaction in bedding material
2	AlF_3	31.3	22.0	30	Fully reacted
3	Alumina	31.8	28.8	9	Fully reacted
4	Alubar 1100, Crushed	31.3	31.3	0	50% reacted
6	Spent refractory brick	31.3	30.6	2	Fully reacted
7	Ramming paste	30.4	*25*	18	Fully reacted**
8	Clayburn DBM	30.4	30.4	0	20% reacted
9	Ramming paste / AlF_3	31.1	*29*	7	Fully reacted
10	OLIBAR	31.5	31.5	0	Fully reacted
11	Alumina	30.6	27.3	11	Fully reacted
12	Alubar 1100, Crushed	30.2	*30.4*	0	50% reacted

**) The distance from the bottom of refractory reference brick to visually reacted material was measured by caliper on the cut cross-section,*
***) Some of the observed reaction depth might be due to discoloration by the binder in the ramming paste.*

4. Discussion

4.1 Test Method

The test method was developed for these experiments, so there is no previous experience with the test method. The objective was to have the same test conditions in each experiment and thereby be able to rank the different materials by the extent of reaction in the brick and/or the barrier.

There are a number of parameters that can influence the final result:

- Temperature/time: Kept fairly constant during all tests. Both are assumed to have a minor influence on the results within the experienced variation band.
- Current/voltage: Varied in some experiment. However, the purpose of the polarization was to aid wetting of the bath and to have a high Na activity environment, which was the situation in a major part of the time in all experiments. The variations are assumed to have a minor influence on the results.
- Bath composition: The same initial bath composition was used in all experiments. A small variation due to difference in charge provided by electrolysis is expected, but it also is assumed to have a minor influence on the results.
- Permeability of bath thorough graphite plate. The amount of bath penetrating through the graphite "membrane" is dependent of the homogeneity and thickness of the plate, as well as the sealing in the edge. The thickness of the plates is given in Table 3 below.

Table 3. Thickness of graphite plates.

Test No.	Thickness [cm]
1	5.00
2	5.20
3	4.20
4	4.20
6	4.06
7	4.10
8	4.10
9	6.30
10	6.59
11	5.60
12	5.34

The reproducibility of Test 3 and Test 4 in runs Test 11 and Test 12, respectively, shows nevertheless that the test method can be used for a qualitative ranking of bedding materials despite the variation in parameters that can influence the result.

4.2 Test Results

The purpose of these tests was to evaluate the performance of bedding materials. The ability to stop bath penetration is the most important property in this context. As it can be seen in Table 2, the chamotte based powders have the best performance. Clayburn DBM and crushed Alubar stop bath in the upper part of the bedding, and Clayburn DBM seems to have a slightly better performance than crushed Alubar. Clayburn DBM contains less SiO_2 than crushed Alubar, which should have the adverse effect on the viscosity of the protective layer formed [1]. However, the mineralogy and the grain size distribution will also influence the result.

Olivine powder, Olibar, also stops the bath penetration, but not as efficiently as the chamotte based powders. The Olibar bedding material gets infiltrated/reacted with bath, but there is no bath attack on the brick underneath. When using alumina as bedding material, the barrier brick reacts and dissolves in the upper area. This is also predictable as no viscous layer is formed nor reaction is expected to take place in the alumina layer. The same applies to ramming paste, but the extent of reaction is cluttered by infiltration of binder into the brick.

The result with spent refractory bricks shows some reaction in the top of the barrier brick. This is probably a reaction between the bedding material and the brick, and not the penetration bath. It is therefore difficult to fully verify the ability of spent refractory bricks to stop bath penetration. Further testing is needed, and the grain size distribution should be varied to assess the suitability of crushed SPL. Furthermore, due to the hazardousness of SPL (spent potlining), HSE considerations must also be considered in this context.

Finally, AlF_3 is not suitable as bedding material. Exposed directly to the refractory brick, SiF_4 gas is formed by the reaction below:

$$4AlF_3 + 3SiO_2 = 2Al_2O_3 + 3SiF_4 \tag{2}$$

Even if AlF_3 is separated from the SiO_2, the neutralization of the basic bath and solid cryolite formation is not efficient in stopping bath penetration.

5. Conclusions

Testing of different bedding materials in lab scale shows that chamotte based powders are considerably better than smelter grade alumina in stopping bath penetration. A chamotte based bedding material will slow down the reaction in the lining, and have a beneficial influence on thermal and dimensional stability of the lining. Use of smelter grade alumina or ramming paste does not stop bath and leads to a more rapid degradation of the barrier bricks.

Use of AlF_3 as bedding material is not recommended as AlF_3 does not react with the basic bath in a way that slows down bath penetration.

6. References

1. Christian Schøning, Tor Grande and Ole-Jacob Siljan, Cathode Refractory Materials for Aluminium Reduction Cells, *Light Metals* 1999, 231-239.