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EXPERIENCES WITH DRY BARRIER POWDER MATERIALS IN ALUMINIUM ELECTROLYSIS CELLS

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Abstract

For several years Hydro Aluminium has conducted plant tests with Dry Barrier Powder materials both in prebake and Søderberg cell cathodes. The present paper reports results from a comprehensive measurement program with monitoring of the performance of more than 60 cells. In addition, autopsies have been performed to study the deterioration mechanisms of Dry Barrier Powders. The investigations have shown that Dry Barrier Powder materials have advantages compared to standard brick linings, giving rise to man-hour productivity increase of the installation, reduced relining costs and more simple logistics. In most cases the operational results of cells lined with Dry Barrier Powders materials are equivalent to that of standard brick-lined cells. However, there are clear indications that Dry Barrier Powder materials may result in higher energy consumption than in standard brick-lined cells. Of the two Dry Barrier Powder types studied, ***Type B*** based on olivine mineral shows the best performance data, whereas the thermally more unstable anorthite based ***Type A*** material may lead to increased cathode voltage drop and energy consumption compared to standard brick-lined cells.

Introduction

The use of Dry Barrier Powders as bottom lining materials in aluminium electrolysis cells is no longer an exotic element in an otherwise conservative industry, but it is a well-established technology. Several types of Dry Barrier Powders are now available on the market, ranging from pure alumina to alumino-silicate, anorthite and olivine-based materials.

The use of Dry Barrier Powders has several advantages compared to standard brick linings, such as:

* *Less time-consuming installation.*
* *Reduced relining cost.*
* *Increased simplicity of logistics.*

In addition, the use of alumina also allows for simplified recirculation of spent pot lining (SPL), either directly as feed stock to the cells or through chemical processes. The main reason for Hydro Aluminium's interest in use of Dry Barrier Powders was to utilise the cost saving potential due to faster installation and shorter cell turn-around. However, it has always been of utmost importance that the reduced costs of relining should not be at the expense of cell performance, i.e. the goal to maintain current efficiency, energy consumption and cell life at the same level as standard brick-lined cells, has always been emphasized.

Testing of Dry Barrier Powders in Hydro Aluminium has been performed at three of our plants with both Søderberg and prebake cells. The amperage of the tested cells ranged from 85 kA to 180 kA, and a total of more than 60 cells have been started with Dry Barrier Powders since the beginning of the tests in 1985. Today about 50 cells are still in operation with Dry Barrier Powder materials within the Hydro Aluminium group. Hydro Aluminium has so far performed experiments with two types of powder materials in reduction cell bottom linings. In addition, a few experiments have been performed with alumina powder as a lining material, but these test cells are still too young for the results to be properly elaborated. The Dry Barrier Powder materials used in Hydro Aluminium today are:

TYPE A: Anorthite-based Dry Barrier Powder material.
TYPE B: Olivine-based Dry Barrier Powder material.

The experiences with ***Type A*** and ***Type B*** Dry Barrier Powder materials will be discussed in the present paper, and the operational results of the test cells will be compared with those of standard brick-lined cells. Table 1 below presents the main physical and chemical data for these two Dry Barrier Powder materials.

Pure olivine consists of solely magnesium oxide and silicon oxide, with a weight ratio $MgO/SiO_2 = 1.33$. Based on the alumina content of ***Type B*** material and a magnesia to silica ratio of 0.82, it is clear that the ***Type B*** Dry Barrier Powder has an additional clay-like substance added to the olivine raw material.

Although it is not obvious from the table, analysis has shown that ***Type A*** material contains no free silica, as compared to almost all other Dry Barrier Powders

Table 1: Physical and chemical characteristics of ***Type A*** and ***Type B*** Dry Barrier Powder materials used in Hydro Aluminium.

Property		TYPE A	TYPE B
Chemical composition			
Al_2O_3	(%)	31.0	11.9
SiO_2	(%)	48.8	43.6
CaO	(%)	14.6	0.2
MgO	(%)	0.7	35.8
Fe_2O_3	(%)	1.0	5.9
Na_2O	(%)	2.7	
Al_2O_3/SiO_2	(wt-ratio)	0.64	0.27
Thermal conductivity			
at 300°C	(W/mK)	0.40	1.6
at 900°C	(W/mK)	0.44	1.5
Installed density	(g/cm^3)	2.0	2.3
Water content*	(%)	2.0	2.0
Fines, $<75 \mu m$	(%)	15	16

* Usually made according to customers' specification.

Table 2: Relative installation costs by use of Dry Barrier Powder materials in aluminium reduction cell bottom linings. All numbers are given in percent, except where otherwise stated.

Item of expenditure	Søderberg	Prebake	Average
Brick cost	100	100	100
Powder cost	170 - 200	100 - 135	150
Insulating cost	100	100	100
Alumina cost	30 - 40	40 - 65	40
Man-hours brick	100	100	100
Man-hours powder	20	15 - 20	20
Savings with powder	**20 - 35**	**35 - 45**	**35**
Reduced shut-down time days	**-***	**0 - 2****	**-**

* All tested Søderberg cells were lined in the relining department.
** Two of the prebake series were lined in position in the potroom, and one series was lined in the relining department.

available on the market. This reduces the potential health hazards of Dry Barrier Powder material dusting during installation and demolition of aluminium electrolysis cells.

Dry Barrier Powder Installation

Brandtzæg et al. (1993) have reported on the experiences with Dry Barrier Powder materials in 125 kA Søderberg cell cathodes. The installation of the material is still mainly performed as described by Brandtzæg et al. A heavy sand compactor is used for compaction of the Dry Barrier Powder. Laboratory tests have shown that the use of a sand compactor proves superior to the use of vibrators mounted on the steel shell casing. This is due to the fact that the Dry Barrier Powders usually are optimized in particle size distribution to enhance installed density. This leads to a poor flow of the dry materials during vibration.

Brandtzæg et al. (1993) have stated that the latest cells are lined with sole Dry Barrier Powder materials as bottom linings. Since this was published, almost all new cells have had an alumina layer in combination with a Dry Barrier Powder layer, the latter being close to the cathode blocks. The use of alumina was mainly based on two criterias; to reduce the total lining cost and to achieve an improved insulation capacity of the bottom lining in the cells ($\lambda_{Al_2O_3}$ at 600°C $\approx$ 0.3 W/mK). Improved insulation was consi-dered to be beneficial from an energy consumption point of view.

Table 2 presents the installation costs for Dry Barrier Powder bottom linings in aluminium electrolysis cells. The data in the table are based on tests performed in two different Søderberg series and three different prebake series in Hydro Aluminium. The numbers are based on a volumetric exchange of materials, i.e. all insulating bricks in the bottom lining are substituted with alumina and all fireclay bricks are substituted with Dry Barrier Powder materials. To compare with standard brick lined cells, the costs of materials and man-power for standard brick-lined cells are set to 100%, and the costs for the Dry Barrier Powder cells are given as a percentage of this value.

From Table 2 it is seen that in most cases Dry Barrier Powders increase the material costs compared to fireclay bricks, whereas the use of alumina reduces material costs considerably compared to standard insulating bricks. Tests performed on a number of cells have clearly shown that the true cost benefits of Dry Barrier Powder materials are closely linked to less man-hours needed during installation of the bottom lining, as reported by Brandtzæg et al. (1993). The data in Table 2 confirm a reduction in man-hours of close to 80% when using Dry Barrier Powders in the bottom lining.

Some of Hydro Aluminium's cell lines do not have a separate relining department. Then the relining of the cells are done while they are in line position, and tests have shown a two-days reduction of shut-down time due to faster installation of the powder materials compared to brick linings. This saving in production loss adds up to more or less the same costs as the total savings from the Dry Barrier Powder material installation in the bottom lining. Hence, it may be concluded that one of the major benefits of Dry Barrier Powders is reduced shut-down time for cells lined in line position.

Lining Temperatures

After installation of new Dry Barrier Powder materials or new lining concepts, the test cells are closely monitored. The monitoring program comprises measurements of bottom lining temperature, heat loss through the cathode shell and follow-up of the cell performance. Hydro

Aluminium has a series of lining designs based on experiences with their Dry Barrier Powder cells. The first cells installed were heavily over-insulated, as reported by Brandtzæg et al. (1993), with bottom lining comprising Dry Barrier Powder and calcium silicate slabs or moler bricks. These cells failed after only about 1000 days of operation, compared to approximately 2200 days as the average life for standard brick-lined cells.

The test cells reported in this paper are all based on either solely Dry Barrier Powder or a combination of Dry Barrier Powder and alumina in the bottom lining.

Shell Bottom Temperatures

Thermocouples are usually installed in two or three different positions in the test cells; on the inside of the bottom steel shell, above the alumina insulation layer and on top of the Dry Barrier Powder underneath the cathode blocks. Figure 1 shows a representative plot of the measured lining temperatures. The thermocouples placed underneath the cathode blocks are usually corroded away after only a few weeks in operation.

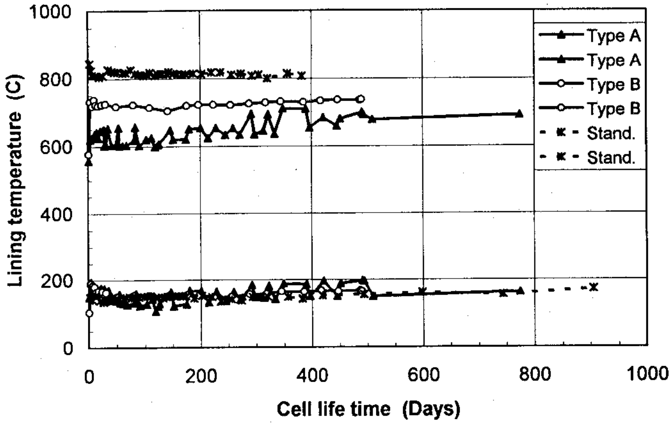

Figure 1: Bottom lining temperatures in 180 kA prebake cells lined with alumina in combination with Dry Barrier Powder materials.

Figure 1 shows the measured temperature on the inside of the shell bottom and above the insulation layer in the cells. The insulation is either alumina powder, for cells lined with Dry Barrier Powder, or moler bricks in standard cells. As can be seen from the figure, the bottom shell temperature is virtually unaffected by the type of insulation used. The temperature is more or less constant, although with a slight increase due to the deterioration of the brick or powder lining above the insulation. The temperature increase measured on the bottom shell seems to be independent of the type of insulation material and whether fireclay bricks or Dry Barrier Powders are used in the cells. The shell bottom temperature seems to solely reflect the thermal properties of the utilized insulation material in the cells, and is rather independent of the refractory material.

The average temperatures measured on top of the insulating materials differ significantly in these cells. Cells lined with standard fireclay bricks have temperatures between the insulation and fireclay materials of about 800 - 820°C. In the Dry Barrier Powder material cells this temperature is lower, usually around 700 - 750°C. However, the type of Dry Barrier Powder material used effects this temperature. ***Type A*** powder starts at a much lower temperature than does the other cell types. The measured lining temperature does, however, increase with increasing cell life time, reflecting the densification and increased thermal conductivity of the bath infiltrated and reacted Dry Barrier Powder. After about 500 days of cell operation, the temperature on top of the alumina insulation has increased by approximately 70°C, and thereafter it seems to stabilize. ***Type B*** powder starts at a temperature of some 90°C higher than ***Type A***, but the increase in temperature is much smaller than in ***Type A***, and after about 500 days of operation the measured temperature on top of the alumina insulation is only 10 - 15°C higher that its starting value. This is comparable to the temperature trend observed for the standard brick-lined cells, and reflects a higher thermal stability of this powder material.

Effect of alumina insulation on bottom shell temperature

After the first successful trials with 100% of Dry Barrier Powder materials in the bottom lining (Brandtzæg et al., 1993), the question concerning reduced materials costs gained interest. As a result of these discussions it was determined to substitute some of the Dry Barrier Powder material with cheap alumina powder. The alumina powder was placed in the bottom of the cell with the Dry Barrier Powder facing the cathode blocks, as it was assumed that the Dry Barrier Powder would react with the penetrating bath and prevent further bath penetration into the insulating alumina layer.

Figure 2 shows the bottom shell temperatures of 130 kA Søderberg cells lined with 100% ***Type A*** Dry Barrier Powder and lined with a combination of 54% ***Type A*** powder and 46% alumina powder. The curves show that although the more insulated cells (with alumina) seem to start at the same temperature level, the shell temperature increases more rapidly in these cells. This causes the opposite effect of what was intended with the extra alumina insulation. The explanation seems to be connected with the fact that increased bottom insulation promotes increased rate and degree of bath penetration in the bottom lining. Hence, higher thermal conductivities of the overall bottom lining are obtained, and as a result the bottom temperatures and the heat loss through the cell bottom increase.

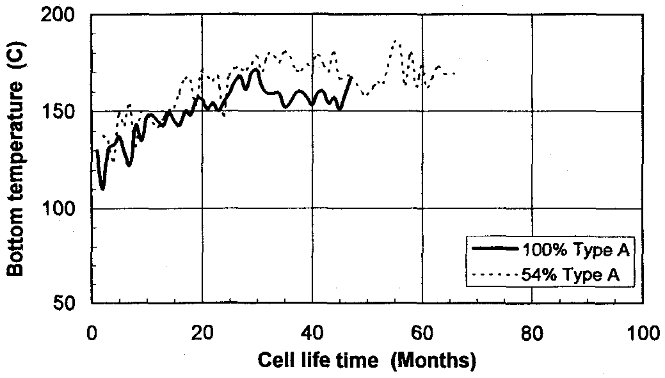

Figure 2: Bottom shell temperature in 130 kA Søderberg cells lined Dry Barrier Powder materials in different lining concepts.

Effect of increased insulation in bottom lining on shell temperature

Results after less than two years of operation with cells lined with Dry Barrier Powder and alumina insulation (see Fig. 2), indicated that the use of alumina as an insulating layer did no harm to the cells. At the same time, focus was put on reduced power consumption of aluminium electrolysis cells and the (beginning) evidence of increased heat loss through the cell bottom of Dry Barrier Powders cells. This led to the conclusion that an increase in the bottom insulation might be beneficial for these cells, and trials were then done with increased height of the alumina insulation underneath the Dry Barrier Powder. Figure 3 shows the effect of increased alumina layer thickness on the observed bottom shell temperatures.

From the figure it is evident that increasing the alumina thickness from 36% to 51% does not severely affect the bottom shell temperatures. The increased alumina thickness seems to be beneficial during the first 6 - 12 months of the cell life, but thereafter the shell temperature is comparable to that of the cells with a lower degree of insulation. Increasing the insulation from 51% to about 58% of the total lining height, however, has the opposite effect from what would be expected. The shell temperatures increase compared to the cells with lower degrees of insulation. This is believed to be due to the fact that the rate of reaction between penetrating bath material and Dry Barrier Powder is increased due to higher lining temperatures in the reaction front. The interfacial temperature between alumina and Dry Barrier Powder is higher than the solidus temperature of the reaction products formed from bath and Dry Barrier Powder. This will result in deeper and more rapid bath penetration into the Dry Barrier Powder materials, and the reaction front occurs beyond the alumina/Dry Barrier Powder interface. This aspect will be further discussed later.

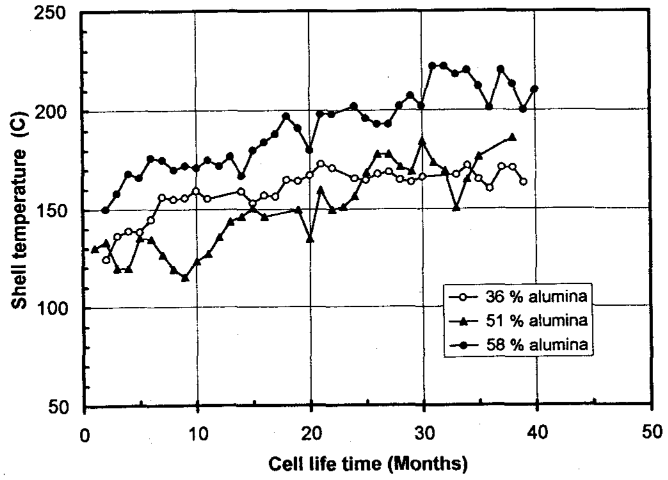

Figure 3: Bottom shell temperature in 130 kA Søderberg cells lined with *Type A* Dry Barrier Powder material with different levels of alumina insulation.

Effect of Dry Barrier Powder type on bottom lining temperatures

Some of the test cells have been equipped with thermocouples above and underneath the alumina layer. The registered temperature drop across the alumina insulation is used as an indicator for the extent of reaction in the Dry Barrier Powder material layer. In Figure 4 the temperature drop across the alumina layer is plotted for cells lined with Dry Barrier Powder of ***Type A*** and ***Type B***. The data indicate that the temperature drop across the alumina for ***Type A*** material severely increases after start-up of the cell. After about 8 - 9 months of operation the temperature drop reaches a maximum value, and thereafter it decreases slowly.

Figure 5 shows the measured penetration depth of bath material into the bottom lining of the same cells as plotted in Figure 4. After about 200 - 300 days of operation the bath material has penetrated the entire depth of the ***Type A*** Dry Barrier Powder material and starts to react with the alumina insulation. This leads to an increase of the thermal conductivity of the powder materials. When only the Dry Barrier Powder is reacting with the bath material, the temperature on the alumina/Dry Barrier interface is increasing. When the alumina starts to react, however, the thermal conductivity of the alumina also increases, and hence the temperature drop across the alumina powder insulation decreases. Measurements of reaction zone temperatures show that these are close to 790 - 810°C in ***Type A*** cell linings.

For ***Type B*** Dry Barrier Powder, the reaction with penetrating bath material does not affect the thermal conductivity of the material, and hence the temperature drop across the alumina remains unchanged. Figure 5 show that the penetration depth in cells lined with ***Type B*** material is not as severe as in ***Type A*** material lined cells. Investigations on cells lined with ***Type B*** material suggest that the penetration depth of the bath material slowly increases through cell life, as shown in Figure 5. The data indicate that after about three years of operation there is still some 30% unreacted Dry Barrier Powder in the cells. Measurements show that the temperature in the reaction

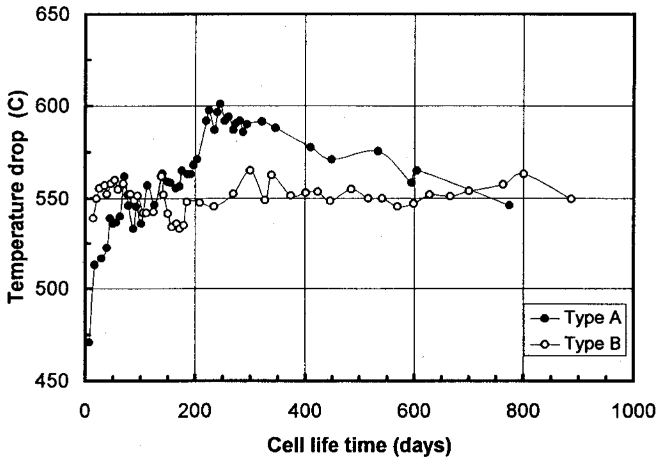

Figure 4: Measured temperature drop across the alumina insulation in 130 kA Søderberg cells lined with *Type A* and *Type B* Dry Barrier Powder materials.

zone is close to the solidus temperature of the reacted material, i.e. about 790 - 830°C. The assumption that the reaction depth is not as severe in ***Type B*** material as in ***Type A*** material, is also supported by the measurements presented in Figure 4. Since a reaction into the alumina layer would create an increase in the thermal conductivity of the alumina powder, a decrease in the observed temperature drop across the alumina would be expected. This is not observed for cells lined with ***Type B*** material.

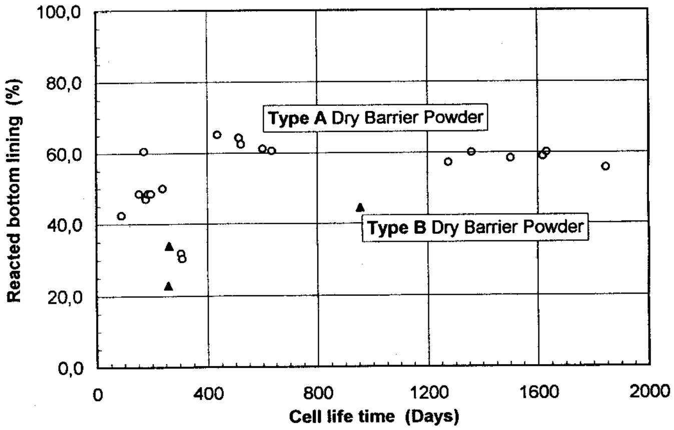

Figure 5: Measured bath penetration depth into bottom linings of 130 kA Søderberg cells lined with *Type A* and *Type B* Dry Barrier Powder materials.

Heat Loss Measurements

The heat loss through the bottom of an electrolysis cell usually represents about 10% of the total heat loss, as reported by Grjotheim and Kvande (1993) and Sørlie and Øye (1992). Hence, only minor savings can be achieved by increasing the bottom insulation. Increased heat loss through the cell bottom may, however, affect cell performance through the build-up of a ridge/bottom ledge on the cathode blocks. This may cause the cathodic voltage drop to increase and thereby give increasing cell voltage and disturbance of the heat balance of the cell. Additionally, ridge formation may effect the metal pad stability of the cell through altering the metal movement (flow pattern).

Figure 6 presents measurements of the heat loss through the bottom shell of a 160 kA prebake cell. The figure indicates that from start-up till about one year of operation, the heat loss through the bottom lining is more or less comparable for cells lined with Dry Barrier Powders and standard brick lining. After about one year of operation the heat loss increases in the **Type A** Dry Barrier Powder lined cells. This is due to the fact that after about one year of operation, measurements in the actual cells show that the bath has penetrated all the way through the Dry Barrier Powder material. Hence, only the alumina insulation maintains the insulation capacity of the lining. Compared to moler bricks used in standard cells, the thermal conductivity of the alumina layer is about 40 - 50% higher, according to data from Hatem et al. (1989).

Investigations of the reaction depth in the powder lined cells show that the height of the reacted material is constant after about one year of operation. Nevertheless, measurements show that the temperature on the alumina/Dry Barrier Powder interface increases in the same period where increasing heat loss through bottom lining is observed. This indicates that even though the height of the reacted powder material does not change, the bath impregnation of the reacted lining continues and leads to increased densification and thermal conductivity of the Dry Barrier Powder material.

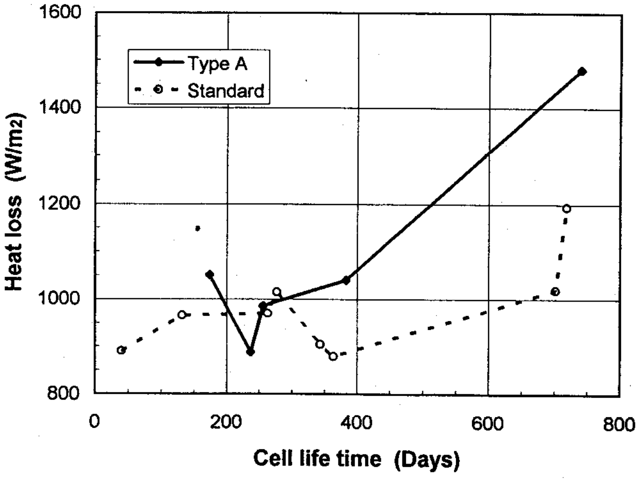

Figure 6: Measured heat loss through the cell bottom in 160 kA prebake cells lined with ***Type A*** Dry Barrier Powder in combination with alumina insulation. For comparison, the same type of data is given for standard brick-lined cells.

Table 3: Obtained operational results of cells with bottom linings based on Dry Barrier Powder in Hydro Aluminium. Operational results for standard brick lined cells are included as a reference.

Series	Standard fireclay brick cells					TYPE A Dry Barrier Powder					TYPE B Dry Barrier Powder				
	Cells #	Age (days)	CE (%)	CVD (mV)	E-cons. (kWh/kg)	Cells #	Age (days)	CE (%)	CVD (mV)	Energy (kWh/kg)	Cells #	Age (days)	CE (%)	CVD (mV)	Energy (kWh/kg)
Sødeberg 1 (85 kA)	11	405	91.8	383	16.0	5	388	93.0	382	15.8	-	-	-	-	-
Søderberg 2 (130 kA)	31	747	91.7	342	15.9	14	549	92.0	357	16.0	5	565	92.1	348	15.8
Prebake 1 (160 kA)	2	670	92.6	395	13.7	1	662	92.7	431	14.1	-	-	-	-	-
Prebake 2 (160 kA)	10	406	92.4	357	14.5	5	401	92.2	356	14.5	-	-	-	-	-
Prebake 3 (180 kA)	5	435	95.5	271	12.5	4	417	95.9	320	12.8	2	269	96.2	274	12.6

Cell Operational Performance

Table 3 presents obtained operational results in cells lined with Dry Barrier Powder materials compared to standard brick lined cells. The results reported are from five different potlines within Hydro Aluminium.

The data presented in Table 3 show that for the small Søderberg cells (85 kA) the operational performance of cells lined with ***Type A*** Dry Barrier Powder is at least as good as the performance of standard brick-lined cells. It is, however, pointed out that the cells are still quite young, and although no signs of weakness have been observed so far, it is still too early to draw a final conclusion concerning cell performance and cell life times.

For the remaining cell types, i.e. the large Søderberg (130 kA) and the prebake cells (160 - 180 kA), the data indicate that the two Dry Barrier Powder materials have somewhat different behaviour concerning the effect on cell operational performance. ***Type A*** Dry Barrier Powder seems to give rise to higher cathode voltage drops (CVD) and higher energy consumption than standard brick-lined cells. The current efficiency is about the same for the two cell types, but in most cases it is a little higher for the Dry Barrier Powder lined cells. ***Type B*** Dry Barrier Powder materials seem to perform more or less identically to standard brick-lined cells. Both cathode voltage drop and energy consumption are the same, and the current efficiency is at least as good in the Dry Barrier Powder lined cells. The test cells are still quite young, and although no signs of weakness have been observed so far, it is too early to put forward any conclusion concerning overall cell performance and cell life times.

In the following chapter, autopsy results and laboratory investigations are used to explain the observed differences in lining temperature, heat loss and cell performance for brick-lined and Dry Barrier Powder lined cell in Hydro Aluminium.

Chemical Reactions in Dry Barrier Powder Materials

The idea behind the Dry Barrier Powders is to create a solid "skull" between the reacted and unreacted lining materials. Seltveit (1984) showed that the reaction between penetrating bath material (sodium fluoride and cryolite) and anorthosite formed new minerals with a solidus temperature above the operating temperature of the aluminium electrolysis cells. This distinguishes the ***Type A*** Dry Barrier Powder material from most of its competitors available on the market, since most other materials are based on alumino-silicate minerals or olivine minerals. Both of these mineral types exhibit a solidus temperature below the operating temperature of the reduction cell. Færøyvik (1994) later found that the true solidus temperature of the sodium fluoride - anorthite - nepheline system was close to 805°C.

When bath materials penetrate the cathode carbon blocks, the chemical composition of the melt can be considered to be basic, according to Siljan (1990) and Sørlie and Øye (1992), among others. This means that the cryolite melt is enriched in sodium fluoride. Equations (1) to (3) below show the expected chemical reactions to take place in electrolysis cell bottom lining when bath material penetrates and reacts with the refractory material. In all cases, sodium fluoride represents the attacking bath, and the refractory lining is assumed to consist of pure anorthite, olivine and mullite, respectively.

$$NaF_{(l)} + CaAl_2Si_2O_{8(s)} = CaF_{2(l)} + 2NaAlSiO_{4(s)} \quad (1)$$

$$6NaF_{(l)} + Mg_2SiO4_{(s)} = 2NaMgF_{3(l)} + Na_4SiO_{4(s)} \quad (2)$$

$$\begin{aligned}78NaF_{(l)} + 17Al_6Si_2O_{13(s)} &= \\ 13Na_3AlF_{6(l)} + 34NaAlSiO_{4(s)} &+ 5NaAl_{11}O_{17(s)} \quad (3)\end{aligned}$$

Bath penetration continues throughout the entire cell life time. This leads to the exposure of already reacted material to "fresh" bath components. Hence, it is no longer the solubility of the fireclay brick or the Dry Barrier

Powder in molten bath that determines the extent of reaction, but rather the solubility of the reaction products in the penetrating bath. Materials based on aluminium silicates are well known for their ability to form highly viscous melts (Siljan, 1990). This means that Dry Barrier Powders based on clay minerals will form the desired viscous melt, and as such they will lower the reaction rate in the bottom lining through reduced diffusivity of bath components through the silica-rich viscous melt. The effect of silica is therefore to increase the melt viscosity and thereby reduce the rate of reaction in the bottom lining. This is supported by the results presented by Schøning (1995) and Tabereaux (1997). Both authors have clearly shown that increased silica content reduces the observed bath impregnation into refractories in laboratory experiments.

Siljan has shown that the solidus temperatures in the molten mixture between pure alumino-silicate (mullite, $3Al_2O_3{\cdot}2SiO_2$) and sodium fluoride-enriched cryolite is approximately 855°C. Færøyvik (1994) found the solidus temperature of the system sodium fluoride - anorthite to be 805°C. Calorimetric investigations of the reaction front material from fireclay bricks exposed to penetrating bath melt in real aluminium production gives solidus temperatures close to 740 - 760°C. For anorthite-based cell linings the solidus temperature is determined to be approximately 800 - 810°C. The observed difference between the pure systems used in laboratory experiments and real lining materials, is of course due to the fact that impurities such as iron oxide, magnesium oxide, calcium oxide, calcium fluoride, etc. are present in the real life systems. The same type of measurement on the reaction zone in olivine-based powder linings indicates a solidus temperature of about 760 - 770°C.

When bath penetrates Dry Barrier Powder materials, the bath attacks the fine grains first and dissolves them. Due to rather severe ingress of bath materials through the first months of operation, as indicated in Figure 5, the bath will penetrate the Dry Barrier Powder without dissolving all of the barrier material. This is evident from laboratory investigations where coarse grains of Dry Barrier Powder material often are detected in the reacted zone. The data presented in Figure 4 also support this assumption. Even though measurements of reacted bottom lining height conclude that the reaction front is stable, the temperature of the reaction front continues to increase. This leads to increased heat loss through the cell bottom and can only be explained through continued bath penetration and densification of the already reacted Dry Barrier Powder lining.

Laboratory results show that ***Type B*** Dry Barrier Powder reacts in the same way as ***Type A*** powder, i.e. in reaction with penetrating bath either calcium fluoride or magnesium fluoride and a "nepheline-like" substance are formed, see equations (1) and (2). ***Type A*** material consists of pure anorthite, both as fine and coarse grains. Bath penetrating and first reacting with the fine-grained material will form a rather low-viscous melt containing fluorides and silicate. In ***Type B*** material, however, the penetrating bath will first react with the fine-grained clay material and hence form a highly viscous melt. The reaction pattern, as described by Thornblad and Grøtnes (1996), will therefore be more like that of fireclay materials, shown in equation (3), than that of pure olivine described in equation (2). The viscous melt formed by reaction between penetrating bath and alumino-silicate materials forms a "protective" molten layer in the reacted lining, and reduces the diffusivity of the bath components.

Figure 7, redrawn from Brandtzæg et al. (1993), shows the calculated thermal conductivity of ***Type A*** Dry Barrier Powder material based on temperature measurements in real cells. The figure shows that as long as the material is not reacted, the thermal conductivity does not differ too much from the thermal conductivity of unreacted powder measured in the laboratory. When the powder is penetrated with bath components, however, the thermal conductivity increases continuously until a stable level is reached. The temperature at which the thermal conductivity increases, is about 800 - 820°C, and this is interpreted as the solidus temperature of the reacted mineral, in good agreement with the results of Færøyvik (1994).

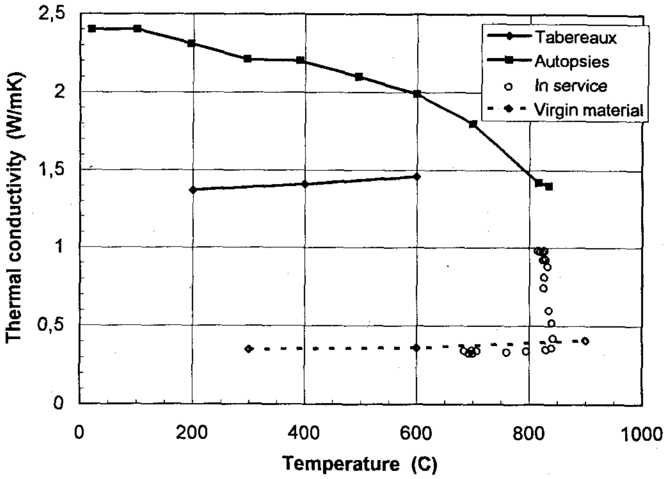

Figure 7: Measured an calculated thermal conductivity for virgin and reacted ***Type A*** Dry Barrier Powder. Redrawn from Brandtzæg et al. (1993), with data from Tabereaux (1997) and laboratory data included.

Unfortunately, the thermocouples do not survive for a long time in the rather corrosive environment of molten bath, and the temperature registrations stopped before a stable thermal conductivity value was obtained. However, in the same figure data are plotted from laboratory investigations of reacted ***Type A*** Dry Barrier Powder material. The figure shows that ***Type A*** material exhibits (as most other Dry Barrier Powders) a severe increase in thermal conductivity when it is exposed to and reacts with penetrating bath. The increase observed during cell life seems to fit well with the thermal conductivity measured on ***Type A*** material from autopsied cells, indicating a thermal conductivity close to 1.4 - 1.5 W/mK for the reacted material. The increase in thermal conductivity will lead to a thermal unstability in the cell lining, and thus cause increased heat loss through the cell bottom and thereby increase the possibilities for ledge formation on the cathode blocks.

Increased ledge formation is believed to be supported by the cell performance data shown in table 3, reflected as increased cathode voltage drop. Differences in measured thermal conductivity from Tabereaux (1997) and our autopsy results are probably due to different measuring techniques and possibly due to different ***Type A*** powder mixtures being used (see Brandtzæg et al. 1993).

The major difference between ***Type A*** and ***Type B*** Dry Barrier Powder materials is, in addition to the chemical composition, the thermal conductivity of the virgin powder material. From Table 2 it can be seen that ***Type B*** has an initial thermal conductivity of about 1.5 W/mK at operating temperatures. This is comparable to the thermal conductivity of fireclay bricks and of reacted ***Type A*** Dry Barrier Powder material. It is hence believed that the benefits of ***Type B*** Dry Barrier Powder material, shown as lower voltage drops and energy consumption compared to ***Type A*** material, are due to the increased thermal stability of cells lined with this material.

Conclusions

Based on the presented data, several conclusions can be drawn with respect to the utilization and cell operational performance when using Dry Barrier Powder materials as bottom linings in aluminium electrolysis cells.

The use of Dry Barrier Powders reduces the time of installation and thereby lowers the installation cost. New results comply with data presented earlier and show reduced man-hour savings of about 80% for the bottom lining. Reduced installation time is of special interest to plants where relining takes place in the cell line, and the shut-down time can be reduced by as much as 48 hours per cell relined. The investigations show that little or no reduction in material costs is obtained by substituting fire-clay bricks for Dry Barrier Powders.

From a working condition and environmental point of view, ***Type A*** Dry Barrier Powder material has the unique benefit that it contains <u>no free silica</u>. This is of importance both during installation and demolition of the cell lining.

Measurements of bottom lining temperatures and height of unreacted powder material show that for ***Type A*** Dry Barrier Powder material the reaction zone seems to reach its "final" depth within the first 6 - 12 months of operation. Thereafter, temperature measurements confirm that continued bath penetration dissolves and reacts with the remaining coarse grains in the material and thereby leads to a densification of the Dry Barrier Powder. The fact that penetrating bath first dissolves and reacts with the fine-grained material is supported through inspections of cup-tests after laboratory investigations. The penetratong will cause reaction and dissolution of the Dry Barrier Powder material until the reaction front reaches the solidus temperature isotherm in the lining. Investigations on cells lined with ***Type B*** Dry Barrier Powder material suggest that the penetration depth of the bath material slowly increases through the cell life, and the data conclude that after about three years of operation there is still some 30% unreacted Dry Barrier Powder in the cells. Temperature measurements show that the temperature in the reaction front is higher than the solidus temperature of the reacted material.

Reactions of Dry Barrier Powders with penetrating bath result in the formation of new mineral phases and relatively low-melting liquids. Calorimetric measurements of solidus temperatures of the reaction zone in Dry Barrier Powder linings indicate that ***Type A*** solidifies at temperatures close to 800 - 820°C when exposed to molten bath (NaF + Na_3AlF_6), whereas ***Type B*** material solidifies at temperatures close to 760 - 770°C. This latter solidus temperature is comparable to that of fireclay materials after reactions in cell linings, reported by Siljan (1995) to be in the range of 740 - 760°C.

The densification of the reacted Dry Barrier Powders causes changes in the thermal conductivity of the materials. Measurements in cell linings and on materials from autopsied cells indicate that ***Type A*** material increases its thermal conductivity close to three times from approximately 0.4 W/mK in virgin material to about 1.4 - 1.5 W/mK in reacted material at cell operating temperatures. Although the same type of data is not yet available for ***Type B*** material, temperature and heat loss measurements indicate that reactions with penetrating bath in this material cause only small (if any) changes in thermal conductivity. From a design and operational point of view, it is obvious that the thermal stability of the lining material after bath exposure is of the utmost importance in order to maintain stable isotherms in the cell lining.

The presented operational data for different types of aluminium electrolysis cells show that no large positive or negative effects can be detected when substituting a standard brick bottom lining with a lining based on either ***Type A*** or ***Type B*** Dry Barrier Powder material. However, the data suggest that the two powder types are not equal, and that care should be taken as to which cell types they are used in.

In <u>high-amperage</u> Søderberg and prebake cells, the data indicate that ***Type A*** material tends to give higher cathode voltage drop (CVD) and higher energy consumption. This is believed to be connected to the observed increased heat loss through the cell bottom, probably giving rise to bottom ledge formation and thereby increasing both cathodic voltage drop and cell voltage. The ***Type B*** material, with its slower rate of reaction and more uniform thermal conductivity, does not seem to give the same effect, thus underlining the importance of thermally stable lining materials.

In <u>low-amperage</u> Søderberg or prebake cells, the lining is much less susceptible to the effects of increased thermal conductivity of reacted Dry Barrier Powder material. From our experiences this is due to the fact that older types of cells usually have quite thick bottom linings and low energy input to the bottom lining. Therefore, in such cells we have not observed any negative effects of ***Type A*** Dry Barrier Powder material.

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