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DRY BARRIER MIX IN REDUCTION CELL CATHODES

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Abstract

Dry barrier mix (DBM) has been successfully tested as a replacement for barrier bricks in several reduction cell technology types and has been adopted as standard practice in all three of the Chinese cell technologies.

DBM reacts with cathodic bath in-situ to form a glass-like barrier which retards the further penetration of bath components, protecting the lighter insulation from contact with the bath. Laboratory "cup tests" and plant trials show that silicate based DBM formulations are more effective than anorthite formulations or conventional refractory aggregates in formation of the glassy barriers. Cell bottom temperatures remain stable over the lifetime of the cell, indicating the barrier formation protects the insulating value. Cell autopsies show partial penetration of the DBM with barrier formation and preservation of the bottom portion of the DBM. Cell lining life is at least equivalent to that of brick barrier cells.

Introduction

Dry granular refractory powders, usually referred to in the industry as dry barrier mixes (DBM), were introduced for use in place of conventional firebricks or chamotte in reduction cell cathodes more than 20 years ago. Several classes of aggregates have been used including some based on the minerals anorthite and olivine as well as standard alumino-silicate refractories. Acceptance in the industry was slow at first, partially because of technical issues with some of the formulations and partially because the DBM products were more costly than the standard refractory linings being used by the major producers. In the last decade use of alumino-silicate based DBM has become standard in the fast growing aluminum industry in China, and today DBM is used for all newly constructed cells of all three of the major Chinese technology design houses. This paper will discuss the performance of DBM in the Chinese cells as well as those of Kaiser Aluminum.

Characteristics of the DBM materials

DBM materials tested in the industry vary considerably in chemistry and particle sizing. Tabereaux and Windfeld reported on the properties of commercially available products [1], but they did not have an olivine based product in their mix. All of the products are meant to be densified during installation in the lining with a typical volume change of around 25%. Table 1 shows the chemistry of some of the products. The two alumino-silicate materials have very different alumina to silica ratios. The anorthite material is characterized by higher calcium content and much finer particle sizing. The olivine material contains a high percentage of magnesium.

Table I: Chemistry and particle size of some of the DBM materials on the market

	Alumino-silicate1	Alumino-silicate2	Anorthite	Olivine
% SiO_2	62	50	31	12
% Al_2O_3	29	42	49	44
% CaO	0.8	1.1	15	0.2
% Fe_2O_3	6	1.3	1.0	6
% MgO	0.8	2.2	0.7	36
% TiO_2	1.5			
%+10 mesh	33	31	0	
%-65 mesh	29	29	55	

Reactions of DBM in the lining

Refractory barriers whether they are composed of fired bricks or DBM are meant to react with infiltrating bath components to form complex compounds which, by virtue of their melting point or viscosity, then retard the further penetration of the bath components. The exact mechanism of this reaction sequence has been the subject of much debate and many publications, especially over the role of the alumina to silica ratio. In 1999 Schoening et.al.[2] attempted to summarize this work and concluded that alumino-silicate refractory with relatively high silica content is probably the best barrier forming material due to the formation of albite when such materials are exposed to fluoride attack. Proshkin et.al.[3] studied the transformations of an alumino-silicate DBM in very young cells (3 and 9 months old), finding mostly nepheline in the transition zone between penetrated and unpenetrated DBM. They proposed that the attacking species are sodium tetrafluoro-aluminate and sodium vapor and concluded that maximum densification of the DBM is vital to its ability to form a barrier. Recently Tschoepe and co workers found the actual barrier boundary layer contains almost no fluoride, and concluded that metallic sodium is the attacking and barrier forming species[4]. It may be that after all the years of study and debate the precise mechanism may still not be known, so the best system can only be decided by field tests in the smelters and especially by actual observation of cut-out cells (autopsy).

Installation Process

The DBM is typically delivered to the relining site in palletized bags or bulk bags. The loose material is placed 18-25% higher than the final designed height of the DBM layer. A wooden form is usually used to contain the loose material as seen in Figure 1.

Figure 1: Wooden form for containment of loose DBM

The DBM is leveled with a screed board and covered with plastic. The surface to be compacted is then covered with thin sheets of fiberboard or plywood. The material is then compacted with a reciprocating sled-type sand compactor (Figure 2). The compacting procedure specified by one supplier calls for three passes of the compactor: first, in a spiraling pattern starting at the corner of the cathode and proceeding toward the center, followed by a reversal then finished with a crossing pattern[5].

Figure 2: Compaction of DBM using a reciprocating sled

Proshkin and co-workers have designed and patented a machine for optimal compaction[6].

Performance in Cells (historic)

The performance of anorthite based DBM in Norway has been extensively reported by Brandtzaeg et.al.[7] and later by Siljan et. al.[8]. Siljan and co-workers reported that the anorthite material gave higher cathode drops (CVD) and higher energy consumption than for standard brick lined cells. The material was found to be penetrated to its entire depth after 200-300 days operation. The penetration rate of an olivine based material was reported to be slower, but penetration continued throughout the life of the cell.

In 1998 Windfeld[9] reported the results of a survey of smelters who had installed a plant trial of DBM material. While little quantitative data was presented, most respondents indicated they considered their trials to be technically a success. The cost of DBM material compared to firebrick at the time deterred some of the respondents from converting their designs to use of DBM.

Cryolite Cup Testing

Kaiser Aluminum used cryolite penetration "cup" tests to choose between several candidate materials presented by vendors. The candidate materials were formed into a mold with a 25 mm cylindrical cavity. The cavity was filled with a mixture of cryolite and sodium fluoride to simulate the high ratio cathodic bath present below the cathode blocks during operation. The firing conditions were 24 hours at 975 degrees C. The material "Alumino-silicate1" was chosen based on its ability as seen in Figure 3 to form the classic black glassy barrier typically seen in standard refractory brick linings. A refractory aggregate of similar particle size to material 1 was also tested and failed to stop the bath penetration or show any sign of barrier formation. An anorthite based barrier also performed very poorly in the cup testing.

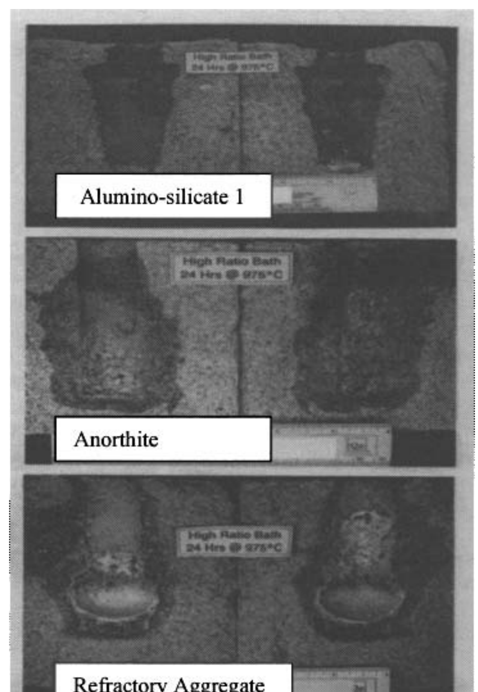

Figure 3: Cup test results for DBM

Performance of DBM in Cells

The DBM "Alumino-silicate1" was introduced in China in 1995 in a 60kA Soderberg pot, and was adopted as standard for 160kA prebake anode pots in 1998. The first trial on a 320kA pot was in

1999. By 2005 DBM became standard for pot construction and reconstruction of all pot series up to and including the 500kA pots.

Aside from the easy installation of the powdered material, Chinese smelters cite the following reasons for converting to DBM material:

- Lower bottom temperatures than with brick lined pots
- Stable bottom temperature over the life of the pots
- Formation of a barrier to bath penetration
- Absorption of cathode dilation which may alleviate upward force in the cathode[10]. In their paper, Qi et.al. do not show the specific data upon which they base this claim. This phenomenon has also been observed in GAMI cells, and investigation is underway to properly quantify the effect.
- Potlife equal to or longer than that achieved with brick lined pots
- Ability to reuse unreacted DBM from relined pots

Bottom temperatures

Thermocouples were placed directly between the bottom insulation and the barrier material in 60kA Soderberg pots. The temperature in the DBM pots was initially lower than the brick lined pots reflecting the lower thermal conductivity of the DBM material. After a few months, as the barriers are formed in both sets of pots, the temperatures converged to a similar value.

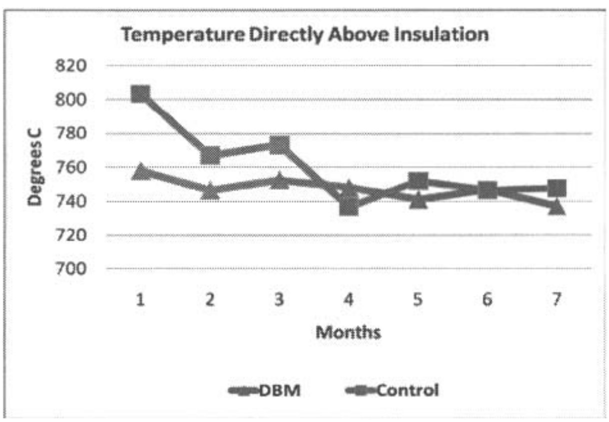

Figure 4: Temperature above insulation; 60kA Soderberg pots

In a longer test in 75kA prebake cells, the temperatures in the DBM cells were also initially lower but took longer to converge as seen in Figure 5. The survival of the thermocouples for five years indicates a viable bath barrier was formed in both sets of cells.

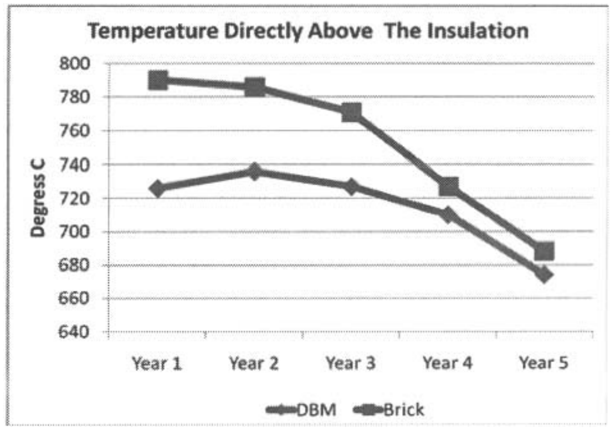

Figure 5: Temperature above insulation 75kA prebake pots

The temperature of the bottom of the potshell was measured on 150kA prebake pots as shown in Figure 6. DBM1 refers to cells where the entire brick layer was replaced by DBM. DBM2 refers to cells where only one of the two layers of brick was replaced by DBM. In both cases the temperature remained below that of the brick lined pots. The steady temperature over the five year period shows the stability of the barriers formed in all three groups of cells.

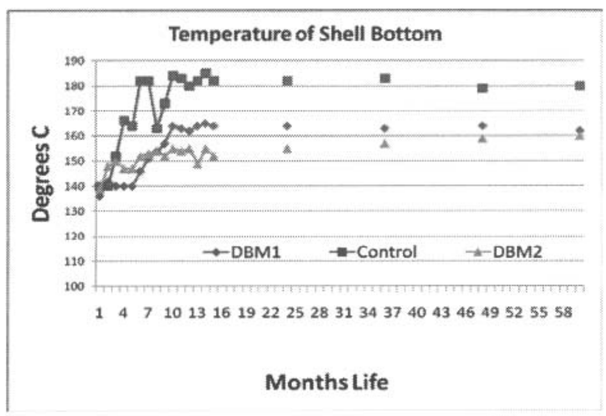

Figure 6: Shell bottom temperature 150kA prebake pots

Operating Parameters:

Current efficiency was measured in the 60 kA Soderberg cells and the 75 kA prebake cells. In both cases the cells containing the DBM had slightly better current efficiency. These results may not be enough to prove statistical significance, but show that current efficiency in the DBM cells is at least equivalent to standard cells

Table II: Current efficiency tests from Chinese smelters

	60kA Soderberg	75kA Prebake
Test length	6 months	3 years
CE DBM pots	91.5	90.4
CE Brick pots	90.4	90.0
Difference	1.1	0.4

Cell Autopsies:

Cell autopsies were performed after about 1000 days operation on 72kA prebake cells lined with DBM (alumino-silicate1) and a refractory aggregate made from used carbon bake flue bricks. Figures 7 and 8 are cross section sketches of the two cells. Figure 7 shows the bath penetration line halfway through the DBM layer, exactly as designed and similar to the typical brick lined pot. Figure 8 shows the bath has penetrated through the entire refractory aggregate thickness and started to react with the insulation below.

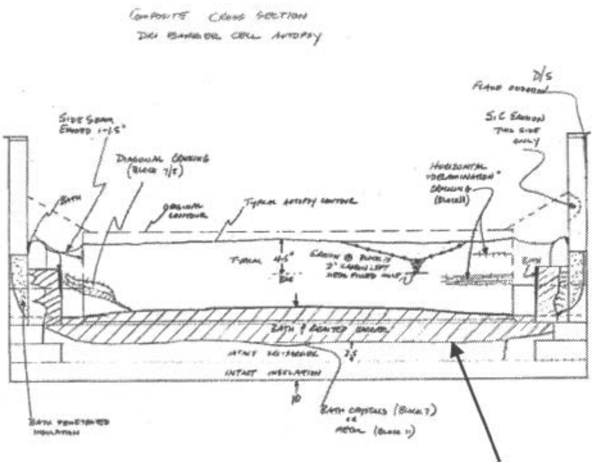

Figure 7: Cross section of DBM lined cell showing barrier formation halfway through refractory. Cell age 1018 days

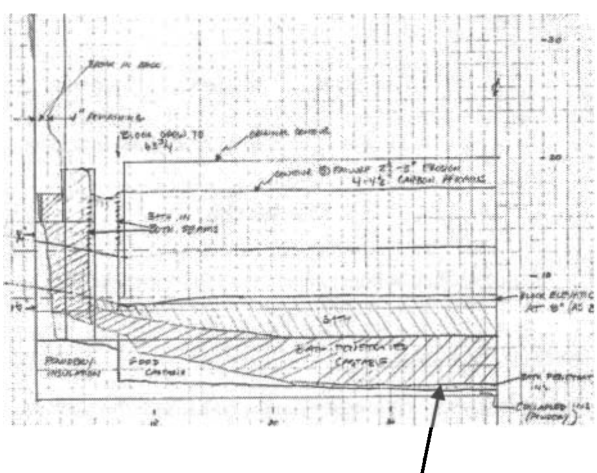

Figure 8: Cross section sketch of cell lined with refractory aggregate (used flue brick). Bath has penetrated through to the insulation. Cell age: 1070 days

Figure 9 shows a picture of the same cell sketched in Figure 7. The unreacted DBM can be clearly seen.

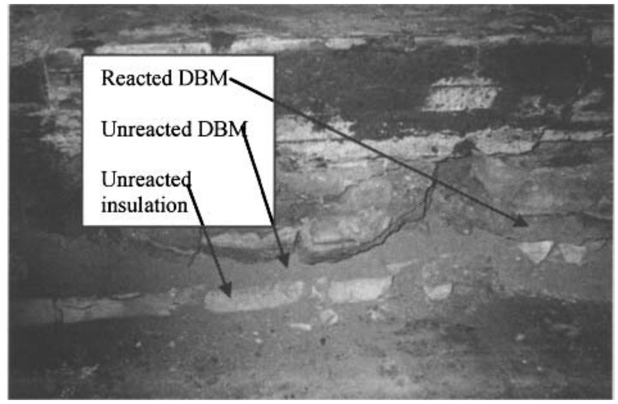

Figure 9: Autopsy of 72kA prebake cell

Cell Life

The relining curve for a 300kA Chinese potline of 240 pots lined with DBM is shown in Figure 10. The median life was around 2200 days, comparable to other technologies using brick linings. Many of the pots in this line were relined according to a maintenance schedule, so the lifetime of the line if run to actual failure would have been greater.

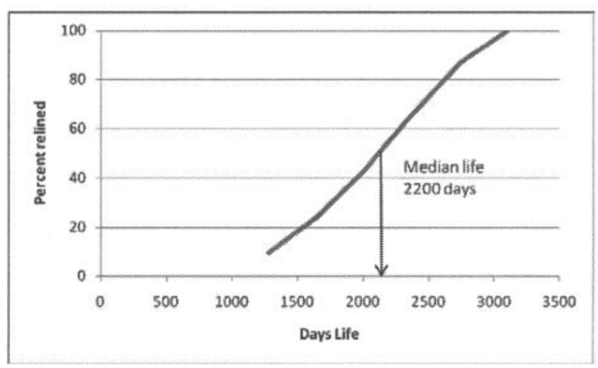

Figure 10: Relining curve for 300kA Chinese potline

Conclusion

DBM ("Alumino-silicate1") has now been adopted as the standard refractory barrier material for all three Chinese technology suppliers and is installed in more than 7000 pots worldwide. It has been proven by bottom temperatures and cell autopsy to form a barrier to the penetration of bath components through the refractory lining, protecting the insulating materials from destruction by bath. Operating parameters and potlife are at least as good as for technologies using brick linings. It has been claimed that DBM may alleviate upward force in cathode linings by absorbing cathode dilation.

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