Development of a Clean Sealing Paste with Improved Electrical Properties

Bénédicte Allard¹, Régis Paulus² and Agathe Thiebault³

 R&D Engineer
R&D Director
CARBONE SAVOIE, Vénissieux, France
Process Engineer, CARBONE SAVOIE, Aigueblanche, France Corresponding author: benedicte.allard@carbone-savoie.fr

Abstract



After the development of clean ramming pastes, Carbone Savoie decided to work on sealing paste product, in order to substitute coal tar based binder pitch and suppress all hazards linked to the PAH components. In parallel to the health and environmental issues, technical developments were also required to improve the properties of standard sealing pastes, mainly the electrical ones to insure a good electrical contact between collector bars and cathode blocks.

There is a new recent interest emerging from the smelters about the replacement of cast-iron sealing for cathode collector bars, linked to operational and organizational considerations as well as to technical optimization of the current distribution in the pot, with new collector bar designs.

This paper intends to present a review of the properties targeted for such contact product and of the different solutions explored to improve the electrical contact resistance between collector bars and cathode blocks, while suppressing coal tar pitch binder and all hazardous components in the product composition.

The conditions of use and the characteristics of the final product achieved are given.

Keywords: Sealing paste, cathode collector bar, clean sealing paste, electrical contact resistance, sealing paste characteristics.

1. Introduction

The electrical contact between the collector bars and the cathode bottom blocks is generally insured by cast-iron poured at around 1300 °C in the gap. This operation is heavy and dangerous and alternative solutions based on pastes and glues have been proposed since many years. Until recently, these solutions were considered worst-performing than the cast-iron. With the recent development of new design of collector bars, with copper inserts, or even full copper bars, the interest in alternative contact material and new sealing operation has grown.

The properties needed for the contact material will be described. A review of the alternative products of the market is presented. The need of a clean product, not based on pitch or hazardous components, with improved electrical properties, has emerged and different solutions have been explored in Carbone Savoie. The impact of the composition on the physico-chemical properties measured is given. The new clean paste produced has been tested at pilot scale.

2. Properties of the Contact Material between Collector Bar and Cathode Block

2.1. Shrinking Behavior

The steel collector bar expands with temperature and its coefficient of thermal expansion of 11×10^{-6} /°C is three or four times larger than the one of carbon or graphite cathode blocks. Copper, more and more widely used as inserts in collector bars, has a coefficient of thermal expansion at 16.6 $\times 10^{-6}$ /°C. The contact material should accommodate these expansions and should shrink with temperature in order to avoid too high stresses on the cathode slots which may lead to cracks [1]. On the other end, the shrinkage of the contact material should not be too high to avoid a gap which would increase the contact resistance. The evaluation of the contact resistance has been performed through experimental simulating benches of various sizes, using small cores [2], as well as complete cathode / bar assemblies in temperature [3, 4].

2.2. Electrical Conductivity

The electrical current is willing to go through the cathode block down to the collector bar. Due to the mechanical pressure applied by the collector bar on the contact material and the cathode aisles, it is commonly observed that the contact resistance is higher at the top of the collector bar than on the sides. The electrical current runs better through the bar sides than through the top of the bar. Consequently the contact material along the sides of the collector bar must be electrically conductive. It is not so important for the contact material at the bottom of the collector bar. The cast-iron electrical resistivity is by far much lower than the one of alternative products: below 0.2 $\mu\Omega$.m at room temperature, up to 1.2 $\mu\Omega$ m at 1000 °C [2]. However it is has been shown that the contact resistance itself is important and can reduce the difference between cast-iron and alternative products.

2.3. Easy to Install, without Risks or Hazards

Another important feature of the contact material concerns its installation. The material should be easy to use and to put in the slot. In this regard, cast-iron is by far leading to the most constraints and risks during the sealing operation, as it needs to be preheated at around 1300 °C and poured liquid in the gap between bar and block, those last ones being preferably also preheated. Thermal shock and block cracking could easily occur on carbon blocks, if there is no preheating of bars and blocks [5].

There are many safety issues linked to the cast-iron sealing operation. Alternative products are much easier to handle, and most of the time do not require preheating. They should not induce other safety issues linked to the presence or emission of hazardous components.

3. Alternative Contact Products between Collector Bars and Cathode Bottom Blocks

The main alternative products to cast-iron on the market are based either on pastes (called sealing pastes or rodding mixes) or on glues /cements. The pastes required a densification by either hand-rammers or double-wheels, whereas the glues can be dropped or pressed manually inside the slot in the gap between the cathode aisle and the collector bar. Some other types of joints, more unusual, will be also presented.

3.1. Sealing Pastes

Sealing paste has been developed in the years 1980's. It could be based on carbon dry aggregates, the most relevant being graphite, in order to obtain a rather low electrical resistivity

same order of magnitude of the gap between collector bar and cathode aisle can be used between HCF80 and the new paste.

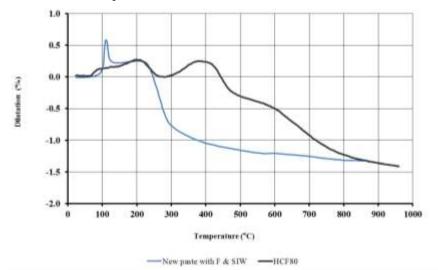


Figure 5: Expansion during baking curve of the new paste based on powder F and SIW binder, compared to the former HCF80.

Industrial production and tests at pilot scale have been performed with the new formulation. As for HCF80, the graphite powder tends to form aggregates during transportation, and a sieving above the gap is necessary.

5. Conclusions

The use of alternative contact material to cast-iron for insuring the electrical contact between cathode blocks and collector bars is increasing with the new designs of collector bars and with the need to find cheaper and less risky sealing process.

A review of the different existing solutions on the market has shown that no product today was both presenting no chemical hazard for the users and having the targeted final properties (low electrical resistivity, shrinkage in temperature). Therefore new studies have been done on new clean binders with different graphite powders and addition of metallic agents.

No formulation of glue enough electrically conductive has been found, but a new sealing paste formulation has been developed, with no hazardous component in the binder, and with much improved electrical resistivity compared to HCF80, with the same type of linear shrinkage with temperature. This product has been tested at pilot scale and will be tested soon in pots.

6. References

- 1. Bénédicte Allard et al., Modelling of collector-bar sealing in cathode blocks with castiron, *Light Metals* 2009, 1097-1102
- 2. Morten Sorlie and Herman Gran, Cathode collector bar-to-cathode contact resistance, *Light Metals* 1992, 779-787.
- 3. Claude Allaire, Effect of collector bars and monolithic mix on thermomechanical stresses induced in the cathode blocks of the aluminum reduction cells, *Light Metals* 1993, 341-348.
- 4. Shinjiro Toda, Katsumi Tayada and Tsutomu Wakasa, Evaluation of contact resistance between rodding mix and collector bar using a 1/5 scale of cathode carbon, *Light Metals* 1999, 603-608.

- 5. Lucio Caruso, Ketil Å. Rye and Morten Sorlie, Experimental comparison of cathode rodding practices, *Light Metals* 2007, 827-831.
- 6. Lise Castonguay and S.K. Nadkarni, Cement for collector bar cathode block joint, *Light Metals* 1990, 539-542.
- 7. J. Mittag et al., Successful experience with glued collector bars, *Light Metals* 1991, 759-762.
- 8. Bettina Hubner, Rainer Sperling, Klaus-Georg Tontsch, Resin-bonded graphite material, method for the production of a resin bonded graphite material and use thereof, *United States Patent Application Publication*, US 2004/0260004 A1, Dec 23 2004.
- 9. Thiago Simões, Márcio Guimarães, Marcelo Assunção, A new material for collector-bar sealing LRM2, *Light Metals 2012*, 1253-1258.
- 10. Chia-Ken Leong and D.D.L. Chung, Pressure electrical contact improved by carbon black paste, *Journal of Electronics Materials*, Vol. 33, No. 3, (2004), 203-206.
- 11. Chia-Ken Leong, Yasuhiro Aoyagi and D.D.L. Chung, Carbon black pastes as coatings for improving thermal gap-filling materials, *Carbon* 44, (2006), 435-440.
- 12. Frank Hiltmann et al., Cathodes for aluminium electrolysis cell with expanded graphite lining, *International Patent Publication*, WO 2007/071392 A2, 28 June 2007.
- 13. Xiangcheng Luo and D.D.L. Chung, Flexible graphite under repeated compression studied by electrical resistance measurements, *Carbon* 39 (2001) 985-990.
- 14. René Van Kaenel and Gualtiero Spinetti, Cathode current collector for a Hall-Héroult cell, *International Patent Publication*, WO 2016/079605 A1, May 26 2016.