Development of a Clean Sealing Paste with Improved Electrical Properties

Bénédicte Allard[1], Régis Paulus[2] and Agathe Thiebault[3]

1. R&D Engineer
2. R&D Director
CARBONE SAVOIE, Vénissieux, France
3. 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 $11x10^{-6}$ /°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 $x10^{-6}$ /°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 µΩ.m at room temperature, up to 1.2 µΩm 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 after baking. Carbone Savoie, for example, has proposed HCF80 sealing paste for years, based on graphite powder. Most of the sealing pastes on the market were different from the ramming pastes, but it could happen that the same grade has been used for both applications: as a ramming paste and a sealing paste.

The main technical functions of both products could be different and sometimes contradictory: Sealing paste specifications include low electrical resistivity and shrinkage in temperature, as mentioned before. For ramming paste, electrical resistivity is much less important, but thermal conductivity has to be adjusted to get a good thermal balance of the pot. To prevent any metal infiltration in the ramming paste or at the interface, it also recommended having a good expanding behavior of the paste.

Therefore most sealing pastes are based on graphite particles, or graphite flakes, mixed with a binder, commonly based on coal-tar pitch family. The binder could be a mixture itself between a liquid binder and a solid binder. The pastes need to be densified mechanically, either by a hand-rammer or a wheel (usually a double wheel that goes in both sides of the gap between cathode slot and collector bar). Ramming temperature could vary from room temperature for cold pastes up to 110 °C for hot rodding mixes. In this last case, people are exposed to toxic fumes during ramming (composed of polycylic aromatic hydrocarbons) and also during preheating.

The typical properties of some sealing pastes of the market are given in Table 1. Paste A is a hot rodding mix that requires a temperature of 120 °C for the densification. Another hot paste B, which was used as a reference in [6], is given for comparison, even if the properties have not been measured in the same lab. Paste C is a cold paste of the market and HCF80 is the former grade of Carbone Savoie which is densified at room temperature. Except paste B, all of them have been measured with the same experimental methods, which will be described later.

Table 1. Characteristics of some sealing pastes with A) hot rodding mix, B) hot rodding mix in [6], C cold paste, HCF80 from Carbone Savoie (typical properties).

Type of paste	A	B [6]	C	HCF80
Green density	1.47	1.45	1.64	1.59
Apparent density after baking	1.38	1.35	1.55	1.34
Electrical resistivity (µΩm)	88.3	103	27.5	40
Compressive strength (MPa)	12	9.5	10	27
Volume shrinkage (%)	- 0.1	-	1.8	4.5
Linear shrinkage (%)	-	0.71	0.1	1.4

The properties of these sealing pastes are quite different, and if we focus on the two main characteristics for these products: electrical resistivity and linear shrinkage, the range of these characteristics is quite high. The electrical resistivity goes from 27 to 103 µΩm, there is a factor four between the lowest and the highest value. For the linear shrinkage, it also varies, from negative value (for A paste, the volume shrinkage only is available and shows an expanding behavior) up to 1.4 %. C paste presents a rather low shrinkage, close to zero. The compressive strength of HCF80 is higher than for the other pastes, but this is not a key point for the use of the paste, as the paste will be compressed by the expansion of the bar.

All these pastes are based on coal-tar pitch binder, and even if the PAH emissions are lower for cold pastes as for the hot pastes, there are still PAH and especially BaP (benzo[a]pyrene) in the composition of the paste which are emitted during ramming and baking of the paste.

3.2. Glues / Cements

Glues have been used as a joint between collector bar and cathode since more than thirty years [4]. The binders are generally based on thermosetting resins, mainly phenolic ones or furannic ones including furfurylic alcohol [6] used alone or with aldehydes. Some are also based on epoxy resins [7, 8].

An advantage of glue/cement is the fact that the application is really easy inside the slot, but it is really important that the curing or hardening of the product is achieved at room temperature in less than 24 hours, in order to allow the handling of the assembly bar/block, without any risk of bar falling.

This constraint implies a careful selection of the resin / catalyst - or hardener – system. Thus the use of any novolak resin, in the phenolic resin family, which is most of the time in solid form, with a liquid solvent, has to be avoided. It requires hexamethylene tetramine (HMTA) hardening agent, or any formol donor, to cure, but always at temperature: 150 °C or even above 200 °C. Resol or resorcinol type resin can cure at room temperature with the respective use of a catalyst or hardener. Furannic resins can also cure at room temperature with a catalyst, but most of the time the reaction is exothermic, and can lead to bubbles formation which may increase the final electrical resistivity of the glue. Epoxy resins require a hardener as well, among them the amines which react at lower temperatures, or the phtalic anhydrides giving reaction at higher temperatures.

To decrease the electrical resistivity of the glue / cement, the filler particles could contain graphite [6], and some metallic additives could be added [7, 9] as for example iron flakes or microspheres. In electronic applications, it has been found that the use of carbon black also improves the electrical contact [10, 11].

On formulations containing a mixture of anthracite and graphite with a furfurylic alcohol – phenolic resin binder [6], the electrical resistivity of glue after baking varies between 37 and 119 μΩm. The lower electrical resistivity is achieved with graphite in the mixture, with a low resin upon solvent ratio together with high catalyst content. The use of carbon black with polyethylene glycol or butyl ether leads to an electrical contact resistivity (between copper blocks) of 16-17 μΩm [10].

With metallic additives, the electrical resistivity could go down to 25 μΩm after baking at 800 °C [7], or even, if the power is only composed of iron with a special binder, down to 0.7 μΩm [11]. This last glue LRM2 is no more commercialized.

Some of these glues present a linear shrinkage during baking [5] allowing standard dimensions of the gap, but some collector bar glues of the market could have an expanding behavior, linked to the formation of bubbles from 200 °C. This type of behavior could induce cracks in carbon blocks. The LRM2 glue presented an expanding behavior up to 500 °C followed by a shrinkage between 500 and 900 °C, and then another expansion up to 1000 °C [11].

Most of these binders give toxic or harmful emissions during setting, with free phenol for example, but also in temperature. Phenol is now classified mutagen class 2, formaldehyde carcinogenic class 2, epoxy resins could contain bisphenol A (reprotoxic class 1B) or other hazardous substances and the hardeners or catalysts of epoxy systems are also generally amines, like ethylene diamine (skin corrosive class 1B). It is difficult to find resin on the market presenting zero hazard with no pictogram.

3.3. Other Solutions

It can be found in the literature other types of contact material, for example expanded graphite [12]. The low electrical resistivity of expanded graphite foils, especially in the plane layer direction, and their compressibility make them a good candidate to absorb the expansion of the bar. The foils are glued to the collector bar or to the cathode block [12]. Under compressive loading, the expanded graphite presents lower electrical resistivity, and this decrease is reversible [13]. The thickness of graphite foil used in [12] is very small. It seems difficult to put only graphite foil between collector bar and cathode: first to find the proper expanded graphite thickness (initial one, and final one under the pressure of the bar), and second to be sure there will be no contact resistance at the interfaces with block and bar. It has been shown that the stress for example at the slot corner could reach 18 MPa after cast-iron pouring at 1300 °C [1]. It will be smaller in case of the thermal expansion of the bar at only 950 °C, but could be easily above several MPa. Expanded graphite reaches very low thickness under 10 bar (1 MPa). This is illustrated in Figure 1 for a typical foil of 12 mm initial thickness: at 10 bar it presents a final thickness of less than 2 mm. Much higher pressure would probably lead to the foil damage and to the block cracking.

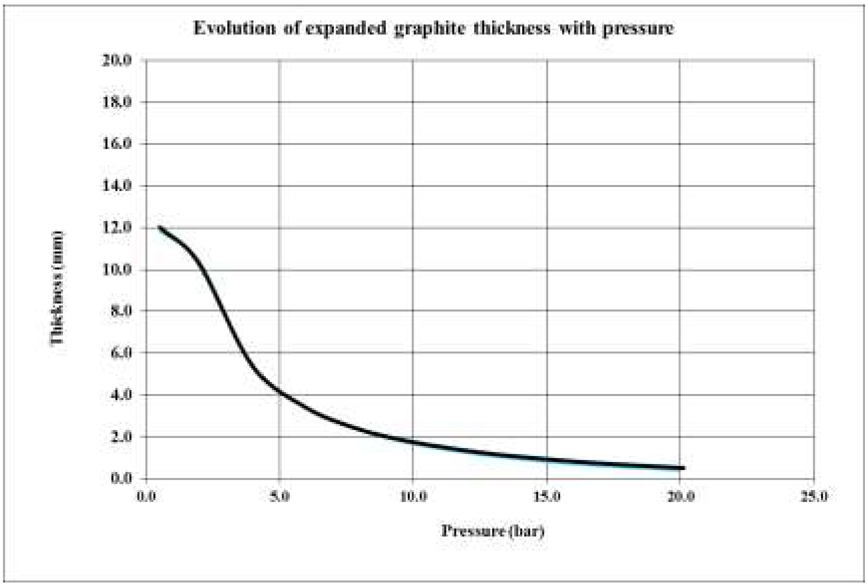

Figure 1. Evolution of expanded graphite thickness with pressure (foil of 12 mm initial thickness).

More recently, direct contact between cathode block and new type of collector bar (based on copper) has also been proposed [14]. The use of electrically conductive glue is also mentioned, as well as conductive interfaces like foam of copper or graphite foils… The impact of the different contact materials on the contact resistance is not evaluated compared to direct contact. The drawback of the direct contact is that it requires very severe tolerances on the bar straightness and roughness, and on the cathode slot as well, to avoid contact resistance at the interface bar / block. The use of an intermediate material that could absorb geometrical defects and bar expansion, without applying too high stresses on the block, is preferable.

4. Development of a New Product

Our objective was to develop a new product, either sealing paste or glue, without any pitch or any hazardous component, with better electrical resistivity or contact resistance than the existing products.

4.1. New Compositions

The development has been made on three different axes:

- The binder nature, to remove all hazards
- The dry materials nature and content
- The use of metallic additives to improve the electrical resistivity.

The binders that have been studied are either soluble in water (named SIW) or hydraulic cements to be used with water. Two types of commercialized hydraulic cements have been selected, that are considered potentially more electrically conductive than standard cements. They will be identified as cements C and S. These cements can stand high temperature, above 1 270 °C for the first one and above 1 700 °C for the second one. No VOC is emitted in temperature. Thanks to the calcium oxide (lime) content, the hardening of the cements starts after 2 or 3 hours, and is completed in less than 5 hours at ambient temperature.

The dry materials are mainly based on two types of graphite, mainly graphite powders, with different grain size distribution and different properties. The graphite content has been varied in the two cements in order to obtain a product similar to glue, which could be poured in the slot.

The metallic additives studied are either copper particles (identified Cu), or iron flakes (Fe), or aluminum powder (Al).

The table 2 below summarizes the main components that have been studied, with their typical density (apparent density for the binders, and real density for the graphite powders).

Table 2. Different components studied in the formulation.

	BINDER			GRAPHITE	
	Soluble in water	Commercial hydraulic cements			
Identification	SIW	C	S	B	F
Apparent density (binder) Real density (graphite)	1.4	1.1	0.9	2.13	2.17

The three binders have been studied with graphite powder B. The amount of powder has been studied, especially for the two cements, on a large range of value from 0 up to 50 %.

The two graphite powders B and F have been studied with SIW water-soluble binder, and the impact of metallic additives as well.

4.2. Experimental Methods of Characterization

4.2.1. Forming

For products like glue, after mixing the components, the mixture was poured in a plastic mold, in order to obtain roughly cylindrical samples of 60 mm diameter and 60 mm length.

In the case of pastes, the same type of equipment which is used to compact ramming paste has been used: the Fischer Sand Rammer equipment with 250 strokes to get samples of 50mm diameter and 50 mm height, or an automatized hand-rammer inside a mold to get larger samples (90 mm diameter and 150 mm height).

For the products based on cements, the densification per ramming gives too much pressure on the sample which either cracks or is damaged. For example, with the Fischer Sand Rammer, the number of strokes should not exceed 100 strokes. Moreover there is no hardening / curing of the cement and the final product has no mechanical resistance. Therefore another type of forming has been used, by pressing under a mechanical press inside a mold (the same one as used with the Fisher Sand Rammer equipment). Preliminary studies have shown that a load of 10 kN with a loading rate of 10 mm/min allows to obtain products with a good density above 1.59. For sealing paste, like the former HCF80 paste, a pressing load of 39 kN is necessary to get a final density similar to the one achieved with the hand-rammer (1.60). At 10 kN, the final density of the HCF80 paste is only 1.48.

4.2.2. Characterization Methods

The apparent density of the green products has been determined. After baking at 1000 °C, the following characteristics have been measured:

- Apparent density
- Volume shrinkage
- Electrical resistivity
- Compressive strength
- Linear expansion or shrinkage curve during baking.

In the case of large samples 90 mm diameter and 150 mm length, a core of 50 mm diameter and 130 mm length has been taken, on which electrical resistivity can be measured according to ISO 11713 standard. For small samples (50 mm diameter, 50 mm length), the electrical resistivity is measured under a mechanical press with the four-point method. Apparent density is measured according to ISO 14427, compressive strength according to ISO 18515 and linear expansion during baking according to ISO 14428 standard.

4.3. Physico-Chemical Properties

4.3.1 Results on Cements

The cements have been prepared with a ratio water / cement of 0.4, which is a typical one and which gave good fluidity of the product. The mixtures were easy to pour in a plastic mould, and the aspect of the products after 24 hours is given on Figure 2. The hardening is done after some hours, with some shrinkage. But 24 hours after, the shrinkage is not enough to extract the products from the molds and the molds had to be cut.

Figure 2. Aspect of cements C (on the left) and S (on the right) with a water to cement ratio of 0.4, and after 24 hours inside a plastic mold of 60 mm diameter.

As said previously, we tried to put powder B in the cements, by mixing powder B with the cement particles before adding water. The percentages of powder B were between 80 and 90 %. With such levels of graphite powder, the mixtures seem homogenous with a good aspect, but the forming is not possible and the hardening is not completed.

Therefore the amount of powder B has been strongly decreased. At 25 % of powder B, the mixture can still be fluid enough to be poured as glues. The aspect of the products after hardening is given on Figure 3. The mixture with cement S exhibits higher porosity.

Figure 3. Aspect of cements C (on the left) and S (on the right) with a water to cement ratio of 0.4, and a content of graphite powder B of 25 %.

Mixtures of both cements with 50 % of graphite powder B have been pressed under the mechanical press at 10 kN, as explained in § 4.2.1., the aspects of the final samples are given in Figure 4.

Figure 4. Aspect of cements C (on the left) and S (on the right) with a water to cement ratio of 0.4, and a content of graphite powder B of 50 %, after pressing under 10 kN.

The green density achieved with the cements is much high without graphite powder, and when adding graphite powder, binder based on cement C allows to get higher green density than cement S. But a strong decrease of green density has been observed on the mixtures with 50 % powder B, with time, with a weight loss of around 4.5 % achieved in two days, probably due to water departure and drying of the paste. Graphite powder is hydrophobic and may contribute to the water departure. The evolution of the green density with time for the cements alone or with 25 % powder has not been evaluated.

The properties at the green stage after forming, and after baking at 1000 °C are given in Table 3. For mixtures with 50 % graphite powder, the values are the average of two samples. HCF80 sealing paste is the reference product, and its typical characteristics are given.

Table 3. Characteristics of the cements with 0-25 and 50 % of graphite powder B, compared to HCF80 typical characteristics (x means non-measurable).

	Cement C			**Cement S**			**HCF80**
% of powder B	**0**	**25**	**50**	**0**	**25**	**50**	
Green density	1.78	1.78	1.58	1.76	1.79	1.54	1.59
Apparent density after baking	1.45	1.51	1.41	1.43	1.51	1.38	1.34
Electrical resistivity (μΩ.m)	x	x	4128	x	x	4462	40
Compressive strength (MPa)	16.6	18.2	10.7	57	59	17.2	22
Volume shrinkage (%)	7.4	5.1	1.7	7.6	2.9	2.4	4.5

The electrical resistivity was too high for the cements and could not be measured except for graphite content of 50 %. Even though they were announced more electrically conductive than other cements of the market, these two cements clearly cannot be used as binders for sealing paste or contact material. By adding graphite powder, the density decreases, the compressive strength and the volume shrinkage as well. But the compressive strength is very high, especially with cement S for 0 and 25 % of graphite powder. This product could be very promising as non-conductive glue.

4.3.2 Results with SIW Water-Soluble Binder

Sealing paste samples based on SIW water-soluble binder have been densified with the Fischer Sand Rammer equipment and the hand-rammer, at ambient temperature, with the two different graphite powders B and F, with in some cases the addition of metallic agents (iron, aluminum and copper particles). The initial percentage of metallic powders was 5 %, but has been increased to try to decrease significantly the final electrical resistivity of the samples. Aluminum has been abandoned as it melts during the baking at 1000 °C. It could have been used in the case of only carbon blocks with the cathode bottom not exceeding 660 °C, but tests at this low baking temperature have not been done.

The different properties obtained at green stage and after baking are given in Table 4. The impact of metallic additives on electrical resistivity is negative, probably because the metallic particles do not link well with the binder which contains some water. The best result is obtained with 20 % iron or copper. Copper gives slightly lower electrical resistivity than iron, but its price is prohibitive. When coming to 40 % iron metallic additive, the densities increase, due to the high density of the additive, but the electrical resistivity increases as well, compared to 20 % additive, the compressive strength decreases, and the volume shrinkage becomes positive. Therefore 20 % additive is probably the best compromise.

The best results are obtained without any metallic additive, but with powder F. In that case the paste obtained is better to former HCF80 sealing paste, with a non-hazardous binder and an improved electrical resistivity (more than 10µΩ.m difference). Therefore this product has been selected to replace definitely HCF80.

Table 4. Characteristics at green stage and after baking of the sealing pastes based on SIW water-soluble binder, with either graphite powder B or F, and with potential addition of metallic additives (Fe: iron, Al: aluminum, Cu: copper).

	New formulations with SIW binder								**HCF 80**
Powder type	**B**							**F**	
Nature of the metallic additive		**Fe**			**Al**	**Cu**			
% of metallic additive	**0**	**5**	**20**	**40**	**5**	**5**	**20**	**0**	**0**
Green density	1.58	1.64	2.06	2.48	1.65	1.68	2.08	1.62	1.59
Apparent density after baking	1.39	1.42	1.77	1.99	1.43	1.47	1.82	1.41	1.34
Electrical resistivity (µΩ.m)	47	55	36	60	550	46	33	28	40
Compressive strength (MPa)	9.4	8.9	16	7.6	3.1	10.2	21.6	17.5	22
Volume shrinkage (%)	7.4	6.1	5.3	-0.8	5.4	6.7	6.7	5.7	4.5

The linear expansion during baking curve of the new paste has been measured on the samples produced with the Fischer Sand Rammer equipment, compared to the one of the HCF80 sealing paste. The linear shrinkage obtained at 1000 °C is about the same, as shown on Figure 5. The same order of magnitude of the gap between collector bar and cathode aisle can be used between HCF80 and the new paste.

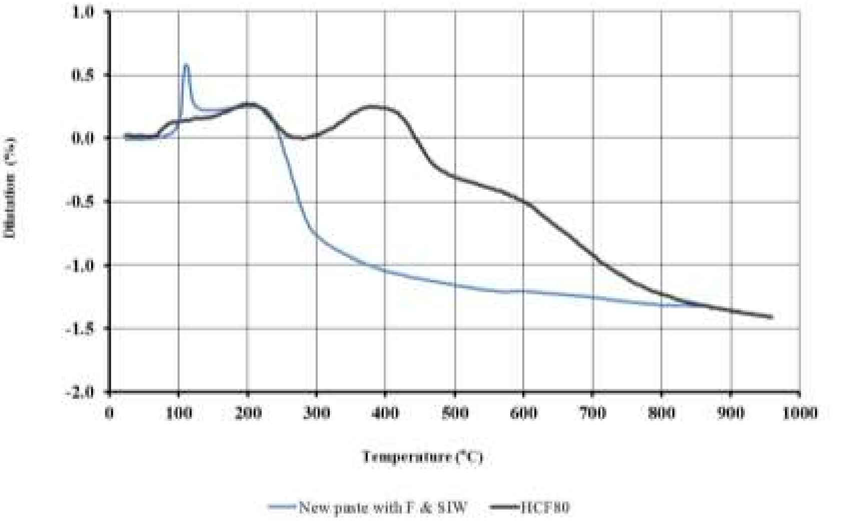

Figure 5: Expansion during baking curve of the new paste based on powder F and SIW binder, compared to the former HCF80.

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 cast-iron, *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.