AD20+: A More Ecofriendly Glue for Aluminum Pot Sides with Improved Properties

Bénédicte Allard[1] and Régis Paulus[2]
1. R&D Engineer
2. R&D Director
CARBONE SAVOIE, Vénissieux, France
Corresponding author: benedicte.allard@carbone-savoie.fr

Abstract

Glues and mortars are commonly used between sidewall blocks and silicon carbide slabs and against the steel shell. Most glues contain hazardous components that are carcinogenic. Mortars, even if less hazardous, usually have poor mechanical and thermal performances. There was a need to develop a new formulation, more ecofriendly and answering more severe constraints on curing time, mechanical and thermal properties. The different requirements for the new glue will be presented. Carbone Savoie has worked in the past on a clean glue formulation, but this glue cannot meet some of the new requirements. The experimental tests out will be described. Main results will focus on hardening time, easiness of spreading on both horizontal and vertical surfaces, mechanical and thermal properties after curing. The characteristics of the new AD20+ glue are compared to the characteristics of other products on the market.

Keywords: Glue, ecofriendly, curing time, mechanical properties, thermal conductivity.

1. Introduction

Glues and mortars are commonly used in the aluminum electrolysis pots at various locations. We will focus in this paper on the use of such products at the sides of the pots, either between sidewall blocks and silicon carbide slabs, or directly against the shell.

These products should answer to more and more severe technical requirements and in addition should be as ecofriendly as possible for the users.

A review of the characteristics needed for the use on the pot sides will be presented, showing the different steps of use and the new specifications that are now required. The existing products of the market, mortars and glues will be described with a focus on their pros and cons. They do not fully comply with the new requirements, and there is a need to improve some specific properties. The experimental tests used to develop a new grade will be described, and the results of the different studies carried out will be given.

2. Different Steps of Use and Characteristics Required for Jointing Materials

2.1. Conditioning and Storage of the Jointing Material

The product should be delivered in small conditioning (25 kg maximum), to facilitate the handling. The amount required per pot is variable depending upon the pot design and if the jointing material is used only between silicon carbide slabs and sidewalls, or also against the shells. But it generally never exceeds 2 tonnes per pot.

In case of glues, the curing can be quicker than for mortars, and the potlife (duration during which the glue can be spread) is limited. Therefore, it is better not to prepare a too high amount of glue.

Storage life should be 6 months minimum, as transportation itself may last one or two months.

2.2. Preparation of the Jointing Material

Whatever the type of product, mortars or glues, they require a mixing operation of generally two components: either a solid in which water will be added (as for mortars) or a powder in which a binder will be added (as for glues). This mixing operation should be easy and short (1 to 3 minutes), and must be done at room temperature (if possible in a wide range of ambient temperature). A typical tool for mixing is shown below. It is the same as for paint, and the diameter can be increased for larger amounts of product. After mixing, the material should be used with no or limited constraint on time, which means that the potlife should be long enough in order not to waste prepared product.

Figure 1. Tool for mixing.

2.3. Spreading of the Jointing Material

There are two types of cases to distinguish: either the jointing material is prepared just before use in pot, or the assemblies are made externally and delivered to the smelters to be installed inside the pots.

For internal use by the smelters on the sides of the pot, the jointing material is used on vertical surfaces only. The support material could be steel, silicon carbide, carbon or graphite, which means different roughness, surface finishing, open porosity, etc. In the case of assemblies manufactured outside of the smelters, the jointing material could be put on horizontal surfaces.

The jointing material should be spread easily with a trowel or a spatula, and should wet the support material. When the thickness of the jointing material must be monitored, the best is to use a notched spatula.

The thickness of the jointing material is typically around 5 mm, and after pressure can reach 2 to 3 mm. In the case of the product placed between the steel shell and the sidewalls, the thickness could be much more important due to the shell deformation and may reach 20 mm in the worst case. For this typical application the final thickness is not uniform all around the pot.

For the spreading on the vertical surfaces, the viscosity of the jointing material is a key parameter: the material should not be too liquid, in order not to flow down, as well as not too viscous to allow covering the whole surface with an easy spreading.

Pressure is put on the assembly after spreading and a sweating of the jointing material can happen. Having such sweating gives some insurance that the cover of the product is homogeneous everywhere, but too much sweating should be avoided to be sure that some product remains at the interface.

2.4. Cleaning of the Tools

The cleaning of the tools must be easy. Water is of course preferred to solvents.

2.5. Hardening / Curing

This is a key step. In case of jointing inside the pot, the hardening / curing should be achieved at room temperature, whereas for external jointing, the curing could be accelerated in temperature with the use of a stove or furnace.

We talk of hardening, when there is a use of a hardener that participates to the chemical reaction, whereas we talk of curing when a catalyst is used that promotes the cross-linking without being directly involved in the reaction.

For jointing inside the pot, stresses due to pot transportation inside the line are much more limited than for external jointing, but the interfaces will be submitted to different types of vibrations, for example during pot ramming. It is important that during this step, the cross-linking of cements or glues is totally completed, in order not to destroy the chemical network obtained by applying moves or vibrations close to the interfaces.

Until now the required hardening / curing duration was typically 24 hours. But the new requirement is a total duration of maximum 12 hours, for a question of shop organization and to allow paste ramming operation after the jointing operation.

There is no real possibility to add a heating facility after jointing in pots, and to achieve a quick cooling to have the sidewalls and blocks back to ambient temperature for the ramming operation. Therefore, the hardening / curing in 12 hours maximum must really be done at room temperature.

2.6. Mechanical Properties after Hardening / Curing

Whatever the cross-linking process is, hardening or curing, the jointing product should present some mechanical resistance at the green stage. In case of assemblies done externally, there are many stresses applied during product loading in trucks and during the transportation by road or by sea, and the assemblies should remain intact. In case of assemblies done inside the pots, the main stresses come from the ramming operation, with the vibrations against the sidewalls. These vibrations are probably the most severe constraints met by the assemblies.
The stresses are mainly shear ones, but could be tensile or compressive or flexural stresses as well.

2.7. Properties During Pot Life

During pot preheating, the jointing product will be baked at temperatures between 300 – 600 °C. It should withstand this range of temperatures and present some oxidation resistance, as some air entrance could happen from the top of the pot.

During pot life, the jointing product should not affect too much the thermal equilibrium of the pot. The ideal would be that it presents the same level of thermal conductivity as the sidewalls or silicon carbide slabs in temperature, and that it does not represent an insulating part. It should also be resistant to aluminum and bath, in case the top of the joint is exposed to the bath / metal interface.

2.8. Health, Safety and Environmental Concerns

The jointing material should contain no carcinogenic product, and if possible non-hazardous components, in order that the jointing operation does not require specific personal protective equipment.

The waste of jointing material should be disposed as common wastes.

2.9. New Specifications

Compared to previous specifications, the main new ones for the jointing materials are the following:

- Clean product with no carcinogenic components
- Possibility of spreading on vertical surfaces as well as horizontal surfaces, with a higher thickness up to 10 mm (or even 20 mm in case of strong shell deformation).
- Short hardening / curing in 12 hours maximum at room temperature.
- Good mechanical resistance to withstand ramming operations with vibrations without any damage of the interface.
- Higher level of thermal conductivity in temperature, close to the one of the sidewalls.

3. Pros and Cons of the Existing Mortars and Glues

Mortars are typically used between shell and sidewalls, and some are also used between silicon carbide slabs and sidewalls. Glues are also proposed, especially at the interface between silicon carbide and carbon or graphite sidewalls.

The advantages and drawback of the existing products are given in the Table 1 hereafter, for the main steps of the process detailed before.

Mortars, based mainly on silicon carbide particles, are easy to use, as they just require water addition. They do not require hazards pictogram, even though they contain sodium silicate or clay at 7 – 10 % in the product, that present hazards for eye, skin or crystalline silica quartz dusts that require precautions during breathing. Their main problems are their long hardening process and poor mechanical properties at green stage. Smelters often complain that unsticking occur during pot ramming or even at high temperatures. It is due to the fact that there is no real crosslinking in mortars like in thermosetting glues. Thermal conductivity values of mortars cannot vary strongly, even with the addition of carbon particles [1], whereas for carbon glues, it can be adjusted through the type of carbon particles used [2].

Glues are generally based on two components. With the presence of a hardener or a catalyst, they can totally cure at room temperature and present high mechanical strength. Their main concern is related to the presence of hazardous components, sometimes carcinogenic. A clean glue was developed by Carbone Savoie, and presented at Light Metals Conference in 2012 [3], This glue was working well if used on horizontal surfaces, but it was not able to be spread on vertical surfaces.

Anyhow, none of the existing glue on the market is known for a hardening / curing in less than 24 hours.

Table 1. Pros and cons of the existing products.

Step of the process	Mortar	Glues
Conditioning (1 or 2 components)	1	2
Storage (months)	12 or 18	12 or 18
Spreading on vertical surfaces with high thickness	OK	OK
Hardening / curing time (hours)	>> 24	24 or 48
Mechanical resistance at green stage	Low	High
HSE concerns	Low	High (CMR)

Therefore, the main challenges with the new specifications were to obtain a hardening / curing in less than 12 hours at room temperature with components as less hazardous as possible.

4. Experimental Tests

The experimental tests used in this development of a new jointing product are described below:

a. Hardening / Curing Time

Trombomat equipment that gives the evolution of apparent viscosity of the product has been described in a previous paper [2]. This type of equipment is a good tool to obtain the duration of hardening or curing, when the viscosity increase with time is completed and reaches a plateau.

In this study, we have worked on small samples poured in a mold (see Figure 2). The mold size is 30 mm diameter and 50 mm high. The hardening or curing of the product is followed by the product hardness at the top and on the sides. When the product is totally hard, it can be extracted from the mold, and used for other characterization tests. Larger molds of 40 and 50 mm diameter have also been used.

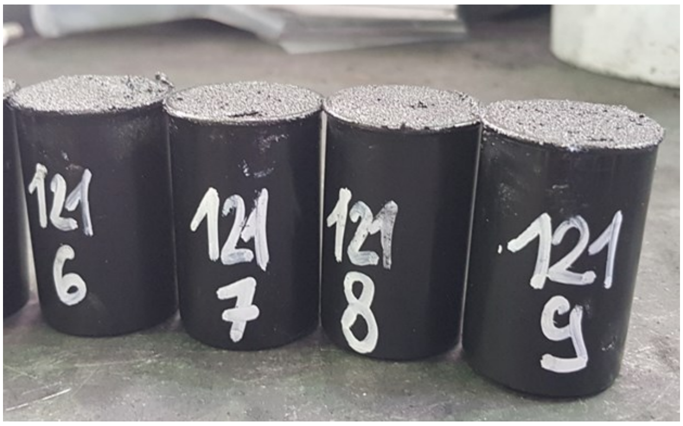

Figure 2. Samples to evaluate hardening / curing time.

b. Spreading Tests

They are performed on carbon materials, graphitic or graphite. We have a bench, presented in [3] to spread horizontally the product, apply some pressure on the assembly and after hardening / curing, to take cores for further analyses (see Figure 3).

Figure 3. Bench for horizontal spreading [3].

In the case of vertical spreading, the same types of slabs have been glued together. Some pressure is applied just after spreading to observe the glue sweating on all sides and especially at the bottom. In the example shown on Figure 4, the sweating at the bottom is rather low.

Figure 4. Vertical spreading on small slabs.

c. Mechanical Tests

Flexural strength is done on the assemblies. A first step is to core samples in the assemblies after hardening / curing. During the coring, shear and torsion stresses are applied, so it is already a positive answer to obtain good cores of 50 mm diameter and 130 mm length.
A second step is to perform three-point bending tests on the cores, in order that the load is applied directly on the jointing material, as shown on Figure 5.

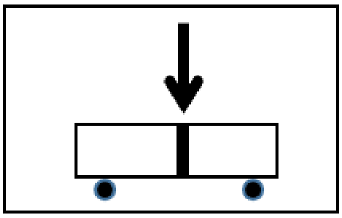

Figure 5. Three-point bending test on the assembly.

This type of test is performed at the green stage, but also after having baked the jointing material. The value of the flexural strength is important, and also the failure pattern, as the breakage could occur in the jointing material (cohesive fracture), or at the interface (adhesive fracture), or even in the carbon material from the slabs.

d. Thermal Conductivity

A new type of equipment acquired by Carbone Savoie has been used: the hot disk, which gives the thermal conductivity and the thermal diffusivity of massive products and of particles as well. This method is based upon the ISO 22007-2: 2008 standard and the last French version NF EN ISO 22007-2: 2015 (F). The principle is based on the transient-plane source technique (TPS) developed by Gustafsson for electronic materials [4] and could apply to any type of materials with a thermal conductivity range from 0.005 to 500 W/m.K and for temperatures from -250 up to 900 °C. The sensor (Figure 6) consists of nickel (electrical conductor) in the shape of a double spiral layered between two thin sheets of electrically insulating materials (Mica or Kapton). The sensor plays two roles: it is both the heat source and the measurement of the temperature increase.

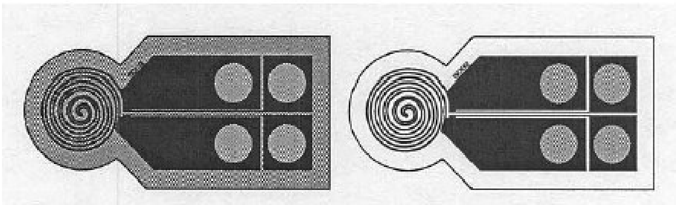

Figure 6. Sensor element with Kapton (left) and Mica (right) [5].

An electrical current going through the sensor induces an increase of temperature between 1 and 3 °C. The resistance of the sensor will increase with the temperature increase and that will induce a voltage increase. An electrical bridge allows measuring the transient resistance increase of the sensor. The sensor is placed between two surfaces of the samples (Figure 7). The shape of the samples is not important, only the surfaces must be flat and parallel to make the hypothesis of a semi-infinite solid.

For our studies, the small cylindrical samples of mortars and glues (30 mm diameter, 50 mm height) have been cut in two parts. We have also studied samples of 40 and 50 mm diameter.

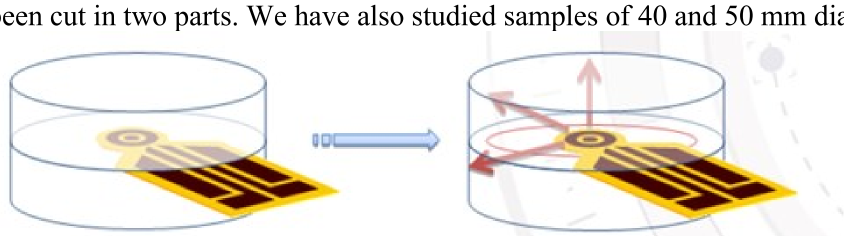

Figure 7. Sensor element location between two surfaces of the sample.

e. Oxidation Resistance

The oxidation resistance is determined through the measurement of weight loss of a sample 22 mm diameter 30 mm long that is submitted to air flow (100 L/h) during one hour at 550 °C.

5. Results

5.1. Samples Studied

Two different mortars from the market have been studied, A and B. For glues, we will compare AD20 glue commercialized by Carbone Savoie, with the clean glue presented by Carbone Savoie in 2012 [1], which will be called "Clean AD20". Also, another type of glue of the market based on furan resin, has been tested, called C.

Besides these products of the market, we have tested different binder systems and various recipes aiming for the least hazardous components and for a curing in less than 12 hours.

5.2. Hardening / Curing Time

For both mortars A and B from the market, there was no real hardening with time: After 16 hours at around 22 °C, the samples in the molds are still soft, even if the top surface is slightly drier and cracks under small pressure (Figure 8b). After 136 hours (close to 6 days), the samples remain soft and cannot be extracted from the molds (Figure 8c).

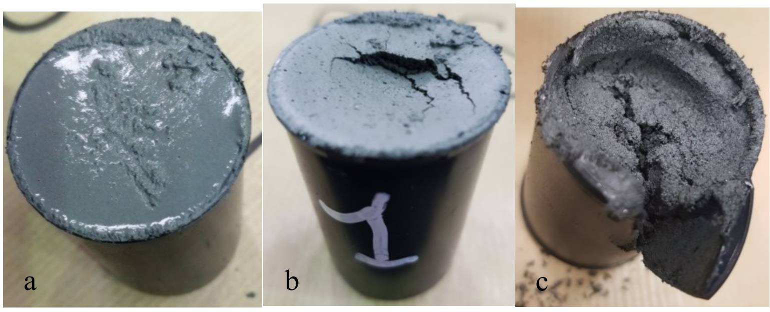

Figure 8. Aspect of the mortar sample: just after preparation a), after 16 hours b) and after 136 hours c).

Parallel assemblies have been glued with these mortars, one on the small bench (Figure 3) with graphitic slabs, and one on industrial gluing bench with one SiC slab and one graphitic block. Whatever the bench and the duration: 12 hours, 24 hours, or 3 days of hardening, no core can be taken in the assemblies: the cores break during coring.

For glues AD20, clean AD20 and C, the observed behavior during curing is quite different between the glues. AD20 cures rather smoothly in 16 – 18 hours at 26 °C with a smooth increase of viscosity. Clean AD20 cures more brutally in roughly 6 hours, whereas C glue cures in more than 40 hours, with an exothermic reaction (for large amounts of glue, typically 4 kg, the glue escapes from the bucket).

Different types of binders have been tried, with no hazardous components, but none of them gives a good curing at room temperature. A gel formation is observed, but no real hardening. As for mortars, the cores taken in assemblies break during coring.

Therefore, a new type of binder has been studied (classified as irritating for skin but not carcinogenic). At 25 °C, the curing of samples occurs within 5 hours (see Figure 9 the aspect obtained after sawing the cured sample). The new glue developed with this binder will be called AD20+.

Figure 9. Aspect of 50 mm diameter sample of AD20+ after curing and sawing.

5.3. Mechanical Tests

Cores have been taken in the assemblies made on our gluing bench, after curing. Three-point bending tests have been performed on these cores with the glue at green stage and after baking the cores at 1 000 °C. Table 2 presents the different results.

Table 2. Flexural strength (MPa) of the different mortars and glues at green stage and after baking at 1 000 °C.

	Mortar A	Mortar B	AD20	Clean AD20	Glue C	AD20+
Green stage	N/A	N/A	7.2	6.0	8.6	12.0
After baking at 1 000 °C	N/A	N/A	3.5	0.2	7.3	0.3

Apart from the mortars, where the cores break during the coring operation, all the glues present good mechanical properties at green stage, and AD20+ glue is the best. After baking at 1 000 °C, the flexural strength decreases a lot, except for C glue which presents surprisingly high resistance. Clean AD20 and AD20+ present the lowest flexural strength after baking, but at least they still stick as some resistance is measured, and their fracture pattern is cohesive.

AD20+ has been tested on vertical surfaces on a model of a corner pot (Figure 10), directly on shell, or on silicon carbide or graphite slabs. Mechanical shocks have been applied on the model with a forklift, the assemblies have remained intact.

Figure 10. Model of a corner of a pot with AD20+ between the shell and graphite slab

5.4. Thermal Conductivity and Thermal Diffusivity

These measurements have been performed only on AD20 and AD20+ glues. For the mortars, it was again not possible to obtain the samples. The results are given in Table 3.

Table 3. Thermal conductivity and diffusivity given by the hot disk at room temperature.

	Thermal conductivity (W/mK)		Thermal diffusivity (mm²/s)	
	green	after baking at 1 000 °C	green	after baking at 1 000 °C
AD20	1.4	1.7	0.8	1.7
AD20+	1.0	1.1	0.8	2.9

The thermal conductivity of AD20+ is slightly lower than the one of AD20, which was not expected, as AD20+ contains graphite particles whereas AD20 contains anthracitic particles. The gain after baking at 1 000 °C is of 20 % for AD20 and 13 % for AD20+. Thermal diffusivity is equivalent between both glues and even higher after baking at 1 000 °C for AD20+, but this could be partially due to its slightly lower density (1.23 versus 1.38 for AD20).

These measurements have been done at room temperature and were quite reproducible. We have not seen any influence of the sample diameter (30 – 40 or 50 mm). In the future these measurements will be done in temperature up to 600 °C.

5.5. Oxidation

Oxidation tests have been performed on both AD20 and AD20+ after baking. They both present the same weight loss of 28 %, certainly not as good as the one of SiC mortars. Anyway it has not been possible to obtain a good core sample of mortar for measurement. The experience of AD20 in pots during years shows that even if it would be an improvement to increase its oxidation resistance, it has not led to any critical problem in pots.

6. Conclusion

The new technical requirements on the jointing material between SiC slabs and carbon or graphite sidewalls ask for a much shorter curing time, together with very good mechanical properties and with ecofriendly or clean products. Usual mortars do not harden or cure at room temperature and cannot stand mechanical shocks or vibrations during paste ramming operation. A new glue AD20+ has been developed, with no carcinogenic components and less hazardous components compared to other glues on the market, which presents very good curing behavior and mechanical properties. Spreading on vertical surfaces in a corner pot model has confirmed that this glue withstands high mechanical shocks.

7. References

72. Javier Olmeda et al., Effect of petroleum (pet) coke additions on the density and thermal conductivity of cement pastes and mortars, *Fuel* 107, 2013, 138-146.
73. Siegfried Wilkening, Carbonaceous gluing pastes, *Light Metals* 1999, 595-602
74. Bénédicte Allard and Régis Paulus, Green, safe and clean carbon products for the aluminum electrolysis pots, *Light Metals* 2012*,* 1247-1252.
75. Silas E. Gustafsson, Transient plane source techniques for thermal conductivity and thermal diffusivity measurements of solid materials, *Rev. Sci. Instrum.* 1991, 62 (3) 797-804.
76. Craig Dixon et al., Transient plane source techniques for measuring thermal properties of silicone materials used in electronic assemblies, *Intl. Journal of Microcircuits and Electronic Packaging,* Vol. 23, No. 4, 2000, 494-500.