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A NEW RAMMING PASTE WITH IMPROVED POTLINING WORKING CONDITIONS

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Abstract

The ramming paste used in the aluminium electrolysis pots has long been a concern regarding health, safety and environment. While the situation has improved over the last 20 years, pastes on the market today still contain either carcinogenic products as PAH components or phenol, or other hazardous components. Health regulations in many regions require substitution of these hazardous components as soon as an acceptable alternative becomes available. A new paste, NeO², has been developed which contains no hazardous component, according to the present regulations. Standard physico-chemical properties of the paste have been studied, with some specific characterizations which will be detailed. This paper will provide a summary of paste developments and provide the latest results achieved with the NeO² paste.

Introduction

Several tons of ramming paste are used per pot, and since the beginning of the aluminium electrolysis process, people have been concerned by the emissions released by the ramming pastes mainly during the densification operation.
These emissions come from the binder of the ramming pastes, which is based on coal tar pitch. As for anode and cathode businesses which also use coal tar pitch binder, the concern is that coal tar pitch releases polycyclic aromatic hydrocarbons (PAH), a number of which are considered as carcinogenic.
Ramming paste is the most hazardous product to which most of the people are exposed during the pot building, as the other products have been either heat-treated, or they are not classified as carcinogenic (cements and mortars for example).
In this paper the historical evolution in the ramming pastes formulation in order to decrease the level of carcinogenic products will be described. The criteria to qualify the potential carcinogenic effects will be also presented. A new ramming paste will then be presented which does not contain any hazardous component according to current regulations. Its main characteristics, standard physico-chemical ones, but also specific ones will be described. Finally the expected impact on the working conditions during the application in pots will be given.

Review of the developments improving working conditions during ramming

In the 1970's, everybody was producing and using hot ramming pastes, based on the same coal tar pitch binder that was used in the anode or cathode manufacture. As a consequence, the working conditions during pot ramming were difficult: the ramming paste, but also the cathode blocks and the sidewalls had to be preheated at 120-140°C, so the paste could be easily densified. People not only worked in a hot atmosphere (and walked on a hot surface), but also they were exposed to a strong release of emissions during the densification. Therefore they were obliged to be well-protected by personal protective equipment.
In the 1990's strong improvements were made on the working conditions: the typical coal tar pitch binder has been modified to decrease its viscosity and allow the densification at much colder temperatures, typically 40°C. That was the development of what was called tepid ramming pastes. The impact on the PAH evolved during ramming operations was quite impressive [1]. Cold ramming pastes, being densified at room temperature (typically 20°C), went further in the easiness of densification conditions.
Among the PAH, which are defined as organic compounds with more than 2 aromatic cycles, about 50 compounds can be present in coal tar pitch, which are considered as more or less carcinogenic. Benzo[a]pyren (BaP), which is classified by the European Union as carcinogenic Category 2 (probably carcinogenic for human) is generally considered as a tracer. The US Environmental Protection Agency (EPA) developed criteria, called the equivalent BaP, the most commonly used being the one proposed in 1994, which takes into account the content of the most hazardous components and their relative weight in the hazard, with BaP being the reference. Table 1 gives the PAH used to calculate the equivalent BaP. Since that time, medical information on the effects of PAH has improved, and a new factor has been developed by INERIS in 2003 [2]: the Equivalent Toxicology Factor ETF, whose calculation is also detailed in Table I.

Table I: Criteria with the relative toxicity factors of the most hazardous PAH according to EPA and INERIS.

	Equiv BaP (EPA 1994)	ETF (INERIS)
Naphtalene		
Fluorene		0.001
Phenantrene		0.001
Anthracene		0.01
Fluoranthene	0.034	0.001
Pyrene		0.001
Benzo(a)anthracene*	0.033	0.1
Chrysene *	0.26	0.01
Benzo(b)fluoranthene*	0.1	0.1
Benzo(k)fluoranthene *	0.01	0.1
Benzo(a)pyrene*	1	1
Benzo(g,h,i)perylene	1	0.01
Dibenzo(a,h)anthracene*	1.4	1
Indeno-pyrene	0.1	0.1

The most hazardous PAH are generally the heaviest ones, which are released as particulates. The lighter ones are mostly released as gas, like naphthalene. Among the 13 PAH considered by INERIS to quantify the toxicity risk, 6 of them (indicated by *) are particulates classified as carcinogenic by the European Union.

The improvements in the ramming paste composition can be clearly illustrated by the decrease of the equivalent BaP or ETF. On the binder alone, when considering hot paste and tepid paste, the equivalent BaP went from roughly 29300 ppm to 21600 ppm, decreasing by 26% [3].

After the move from hot to tepid and cold pastes, there have been some developments in the mid 1990's to substitute resin binders for coal tar binders. The best resin candidate to replace coal tar pitch is phenolic resin [4]. But phenol is also a hazardous component which is now classified as carcinogenic. It does not allow the removal of all the carcinogenic compounds from the paste composition. Moreover the final characteristics of the ramming paste show that the shrinkage of the paste during its baking up to 1000°C, could be very important and may induce a risk of infiltration in the pot [5].

In 2002, a new family of ramming paste was introduced on the market, called ecofriendly (EF) [3]. The binder, still issued from coal tar pitch, was specially treated to decrease significantly the most dangerous PAH, and especially BaP. Table II shows the decrease in ETF when moving from tepid and cold pastes to the EF family.

Table II: Typical ETF for the different types of ramming paste.

Type of paste	Tepid	Cold	Tepid EF	Cold EF
ETF (ppm)	2500	2300	300	360

The difference of ETF between tepid and cold ramming pastes is not considered as significant, because these average values come from a small number of values. The EF family shows a decrease in the ETF by a factor 6 or 7. This improvement has also been demonstrated by emission measurements during ramming operation and during laboratory baking. In parallel, the final characteristics of the EF ramming pastes were similar to those of standard pastes.

Since then, the EC Directive 2004/107/CE of European Parliament was published in Official Journal dated 26.1.2005, and asked for substitution of carcinogenic products when possible. There is an obligation of justification towards local authorities when carcinogenic products are used.

As the EF family still contains PAH components with a non-null ETF, there is still a need to medically follow-up the use of these products. They still require individual protective equipment and a specific labelling showing the hazards for the users. The situation is the same for pastes with resin binders.

Characteristics of the new paste developed

Chemical Hazards

The new ramming paste developed, called NeO^2, does not contain any carcinogenic component classified by the European regulations. It is not based on a resin binder or on a coal tar or petroleum tar binder. The PAH profile of the ramming paste (Table III) shows that any PAH present was below the detection limit of the method used, compared to some recent batches of standard and EF pastes.

In the case of the new paste, no carcinogenic product is present, and in fact no hazardous component is used. The Safety Data Sheet of each raw material does not mention any hazardous ingredient.

Table III: PAH profile of the new paste compared to tepid standard and EF ramming pastes.
Values for NeO2 are the detection limits.

In ppm	**Tepid paste**	**Tepid EF paste**	**NeO^2 paste**
Naphtalene	400	7000	<58.7
Fluorene	2300	2500	<5.9
Phenantrene	6900	5100	<11.7
Anthracene	600	500	<2.9
Fluoranthene	4400	2200	<29.4
Pyrene	2500	1200	<11.7
Benzo(a)anthracene*	800	100	<11.8
Chrysene *	800	100	<29.4
Benzo(b)fluoranthene*	1100	100	<11.8
Benzo(k)fluoranthene *	500	43	<5.9
Benzo(a)pyrene*	**1200**	**100**	**<5.9**
Benzo(g,h,i)perylene	800	100	<11.8
Dibenzo(a,h)anthracene*	1700	200	<23.5
Indeno-pyrene	900	100	<117.4

Investigation on the components released during baking up to 1000°C is on the way. It has to be recalled that petroleum tar binders, which do not release PAH at ambient temperature, emit a high amount of PAH, especially BaP, during baking [3], almost 30 times more than a hot ramming paste! In NeO^2 paste, among the list of 14 compounds of PAH, only naphthalene is detected at elevated temperature.

Therefore the use of this new paste will modify significantly the working conditions in the pot, as we will see later.

Standard physico-chemical characteristics

The standard physico-chemical characteristics of the new paste have been determined, in order to compare them to those of standard and ecofriendly ramming pastes, all of them being purely anthracitic grades.

The samples have been densified with a hand-rammer at 20°C for the new paste and some cold pastes. The tepid pastes have been densified at 40°C.

Table IV summarizes the green density on samples 90 mm in diameter and 150 mm long, and the main properties after baking at 1000°C: volumic expansion and crushing strength.

Table IV: Typical characteristics of the new paste compared to standard and ecofriendly ones, tepid or cold ones.

	NeO^2	20°C std paste	20°C EF paste	40°C std paste	40°C EF paste
Green density	1.62	1.60	1.59	1.59	1.59
Baked density	1.39	1.44	1.45	1.44	1.46
Volumic expansion (%)	2.6	1.5	1.4	1.8	1.1
Crushing strength (MPa)	19	17	18	23	24

The volumic expansion, that represents the difference of volume between the green stage and the densified stage, is a key parameter for the performance of pot. If this volumic expansion is negative, it means that the paste will shrink during the pot preheating, and the risk of metal infiltration is very high. As can be seen in Table IV, the new paste presents a typical green density close to that of the other pastes, a good volumic expansion and a crushing strength also of the same order of magnitude.

Specific characteristics

Rammability index and temperature window from the Fischer Sand rammer (FSR)

The rammability index is determined with a Fischer rammer equipment which has been adapted in order to perform automatically 250 strokes and to measure the geometrical density of the ramming paste for each stroke (see Figure 1).

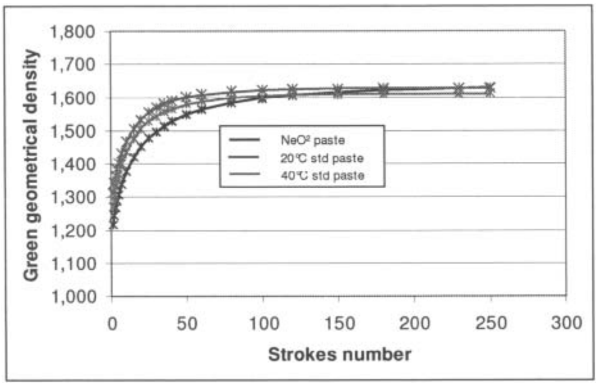


Figure 1: Examples of density curves obtained for the new paste and for the standard pastes.

The paste is densified at 20°C in a mould to get a sample of 50 mm in diameter and 50 mm high. From the densification curve, the maximum green density can be determined (asymptotic value), and also the rammability index N2. This index is calculated by assuming a Weibull's law, as detailed in the ISO standard 17544:2004.

When the value of N2 is very high, it corresponds to a dry paste, which requires a lot of energy to be densified. If the value of N2 is very low, it corresponds to a very wet paste, which is easily densified. Table V shows that the new paste presents a higher rammability index than most of the standard pastes presented here, so may requires slightly higher energy (longer ramming time) to get densified. The maximum green density is also higher.

Table V: Typical rammability index N2 and maximum green density D max, for different ramming pastes

	NeO²	20°C std paste	20°C EF paste	40°C std paste
N2 (strokes)	72	51	44	48
D max	1.641	1.622	1.620	1.605

The ISO standard 17544 considers the range of ramming temperature, where the rammability index N2 is comprised between 65 and 130, and defined it as the temperature window of the paste, even if it is not really in accordance with the practical temperature window determined from the characteristics of hand-rammed pastes. Figure 2 shows the evolution of N2 versus ramming temperature for NeO² and a 20°C standard cold ramming paste. N2 is comprised between 65 and 130 for a range of temperature of [11-35°C] for NeO², and for a range [2-11°C] for a cold ramming paste. This is due to the fact that the rammability index is generally higher than the one of standard paste, especially below 30°C, whereas the standard paste exhibits very low values of N2, even at low temperatures. It seems that the temperature window is thus larger for the new paste. But another study will be made on larger samples, to check the characteristics for different ramming temperatures, and determine the practical temperature window.

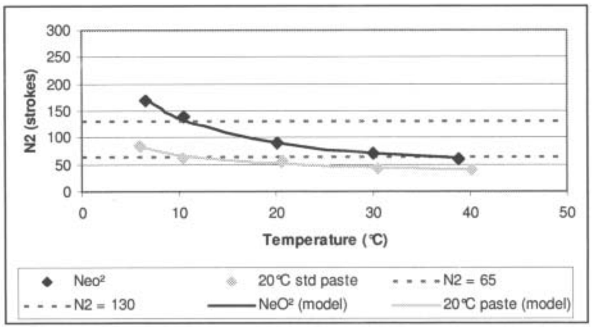


Figure 2: Evolution of the rammability index N2 versus temperature for NeO² and a 20°C paste.

Expansion during baking curve

Besides the volumic expansion, it is important to follow the linear expansion curve of a ramming paste versus temperature, to clearly detect the dimensional evolution that will be met in pot during the preheating.

The test is performed on the sample densified by the Fischer Sand Rammer. The linear evolution of the sample versus temperature is recorded with a displacement gauge.

Figure 3 shows the curve for the new paste compared to typical ramming paste.

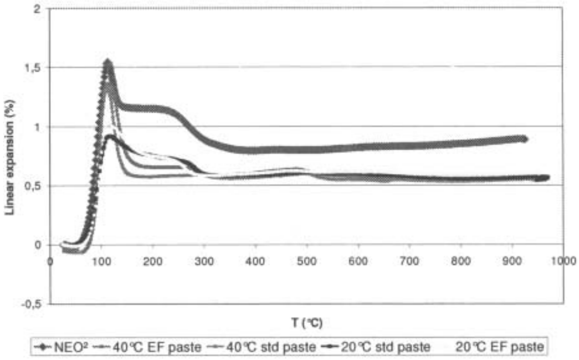


Figure 3: Linear expansion during baking curve for NeO², 40°C pastes (EF and standard), 20°C pastes (EF and standard).

The curve of the new paste exhibits a peak above 100°C, as the other paste, but the shrinkage after the peak is smaller, and above 500°C (the typical cokefaction temperature of the coal tar binder), the shrinkage which is already very low for the considered pastes, is even a small expansion for NeO² paste. This could be result in a decrease in the risk of metal infiltration in the pot.

Thermal conductivity and oxidation resistance

These are some specific characteristics that need to be determined to predict the thermal conductivity of the pot side and the frozen bath ledge position, or to confirm that the paste could stand heating without being oxidised, for example in case of pot preheating with gas burners. These two characteristics are the same for all anthracitic grades, whatever ramming temperature is used. They could be modified for semi-graphitic grades: typically the thermal conductivity is increased by a factor 2, and the oxidation resistance is also slightly increased. Compared to the average values for anthracitic pastes, NeO² presents the same level of thermal conductivity, as shown on Table VI, and a slightly better oxidation resistance.

Table VI: Thermal conductivity (in W/m.K) and weight loss per oxidation (in %)

	NeO² paste	Anthracitic pastes
Thermal conductivity	5.6	6.0
Weight loss per oxidation	6.0	9.5

Ageing

Typical ramming pastes present a shelf life of several months. Above this shelf life, due to the volatile departure from the binder, there is a risk of an evolution of the paste characteristics: mainly a drying of the paste (the rammability index increases) and a decrease of the volumic expansion. The ageing of the new paste has been followed on 25kg bags stored at ambient temperature. Each month 2 bags were analyzed and the average values of the rammability index and the volumic expansion are given in Figures 4 and 5. After 12 months, the paste still presents a volumic expansion above 1%.

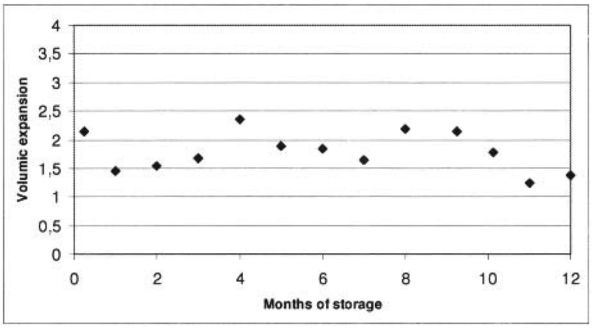


Figure 4: Evolution of the rammability index versus the months of storage, for the new paste.

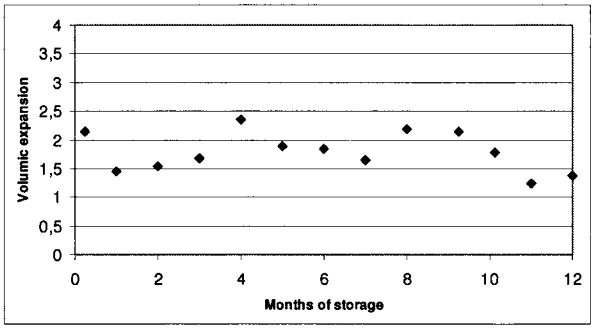
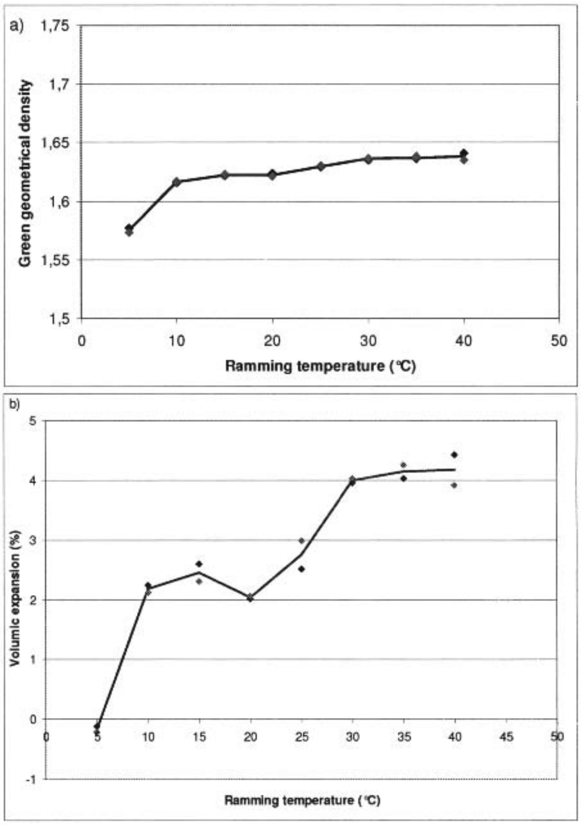


Figure 5: Evolution of the volumic expansion versus the months of storage, for the new paste.

Temperature window

The practical temperature window inside which the ramming paste could be densified and still exhibit good properties is determined on large samples (90 mm in diameter and 150 mm long). Different ramming temperatures have been studied from 5 to 40°C, each 5°C. Two samples were densified and baked at 1000°C for each case.



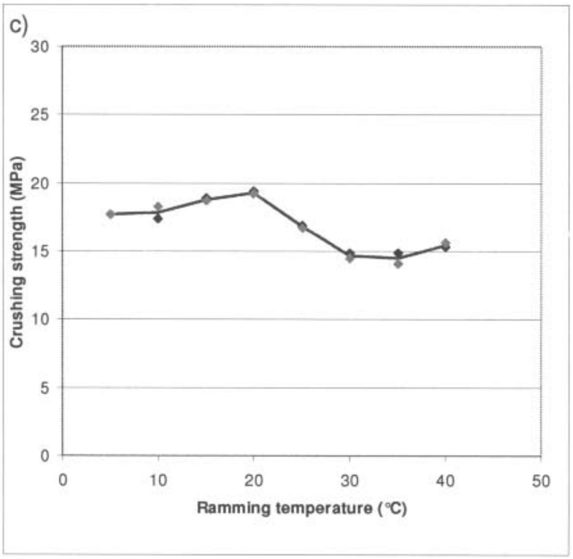


Figure 6: Evolution of properties versus the ramming temperature: a) green density, b) volumic expansion, c) crushing strength.

Even if the nominal ramming temperature of the paste is 20°C, it appears that it could be densified between 10 and 40°C, and still presents good volumic expansion and crushing strength (Figure 6). Above 30°C, the volumic expansion is higher, in accordance with the lower crushing strength, but the average levels are still correct. At 5°C, the volumic expansion is negative, which could be detrimental for the performance in the pot.

Evolution of crushing strength versus baking temperature

The ramming paste has been baked between 300 and 600°C, and the crushing strength has been measured at room temperature after cooling. This test is not as representative as a crushing strength measured at the baking temperature, but it gives an idea of the evolution of the mechanical properties of the paste at different steps of baking.

The results are illustrated in Figure 7, in comparison with various pastes. For NeO^2, the crushing strength is nearly constant since the baking temperature of 300°C, whereas for the other pastes, it increases from 500°C, which corresponds to the binder cokefaction. In the case of NeO^2, the binder cokefaction may occur at a lower temperature than 300°C. Some further tests will be performed to check this hypothesis.

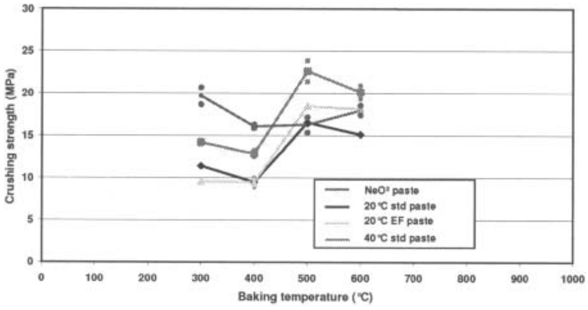


Figure 7: Evolution of the crushing strength measured at room temperature, versus the baking temperature, for the different standard and EF ramming pastes

Application in pots

Impact on the working conditions

The use of the new paste could improve significantly the working conditions. The main point is the absence of carcinogenic products, and more generally of hazardous products in the composition of the ramming paste according to current regulations. It could be used by itself without respiratory masks. It does not smell, which means that the protective clothes will not be impregnated by a strong smell, as with coal tar pitch or resin binders. In addition to the suppression of the risk of breathing hazardous compounds, the risk of pitch contact with skin, which requires efficient protection [6] is also removed.

Due to its composition, the ramming paste could be destroyed as a common waste. It means that there is no more need to send it to special incineration station.

The working temperature window is rather wide, which will be more convenient for the blocks / paste and tool preparation before ramming. Compared to typical 20°C ramming paste, the shelf life of the paste is larger: 11 months at least, instead of 8.

The physico-chemical characteristics of the paste are in line with those of the other pastes, thus with a good volumic expansion, and a promising linear expansion curve during baking. The crushing strength is intermediate, and not too high to avoid applying stresses on the cathode blocks. The rammability index is higher than those of the main pastes that have been presented for comparison, and closer to some other pastes on the market. It means it may need a slightly longer ramming time than the reference pastes, but similar to the conditions used for other commercialized pastes.

Experience in pots

Several industrial production batches of Neo^2 paste have been made, and two pots are now running in two different smelters, in two different pot technologies. The ramming operation was similar to the usual one, and the total ramming duration was found to be about the same, not significantly increased.

Measurements of emission have been done during ramming. The results are not yet available, but will be compiled in the next future.

Conclusion

In accordance with the EC Directive 2004/107/CE of European Parliament that asks for substitutes to carcinogenic compounds whenever it is possible, the new ramming paste NeO^2 appears to be a good alternative to the usual ramming pastes, as it does not contain any carcinogenic product, neither any hazardous product, according to current regulations. The working conditions during ramming should be easier, with the removal of the masks. The fact that the paste does not smell, can be densified in a rather large temperature window, can be stored during at least 11 months, and can be treated as a common waste are some of the advantages which differentiates the paste from the standard ones. The physico-chemical characteristics are maintained and sometimes improved such as the expansion during baking curve, with a slight expansion during 500 and 950°C. The evolution of crushing strength with baking temperature tends to be a plateau, different from the increase observed with the other pastes. Future work will include measurement of compressive strength at the baking temperature to be able to better predict the paste mechanical behaviour in the pots.

Results from pots are expected regarding the emissions measurements during ramming and the follow-up of the pot performances.

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