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EXPERIMENTAL RESEARCH FOR THE PRODUCTION OF CASTING REFRACTORY MATERIALS WITH CHEMICAL BINDING

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In this paper the authors are presenting the technology of obtaining important landmarks which compose the gas bubbling assembly in steel, using a chemical binder. The used raw materials, the chemical and particle size analysis of the raw materials, the recipes of the raw materials, but also the qualitative analysis of the obtained products are presented. The features of the gas bubbling assembly are presented compared with both Romanian and international rules.

The authors are also presenting the economic advantages of making the components of the bubbling assembly through the technology of casting-vibration, using chemical binder.

Keywords: refractory products, casting-vibration, chemical binder, steel stirring, porous plug

1. Introduction

The development and modernization of technologies in the field of steel and metallurgy in general has led to particularly severe demands on refractory products used in installations and aggregates [1-3] in the last decades of the last century. It is necessary to reorient the production of refractory materials in two important directions, namely:

- the need to produce high quality products with increased durability in operation, in the conditions of increasing working temperatures and increasing the aggressive attack on the refractory material and

-the needs to make compact products with very large dimensions and/or particularly complicated shapes,which could no longer be achieved by classical shaping technologies in superior quality conditions.

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For the silico-aluminum refractory products (from the SiO_2 -Al_2O_3 system, Fig. 1), the condition of the qualitative increase meant the achievement of products with a high alumina (Al_2O_3) content [1, 2, 4-6]

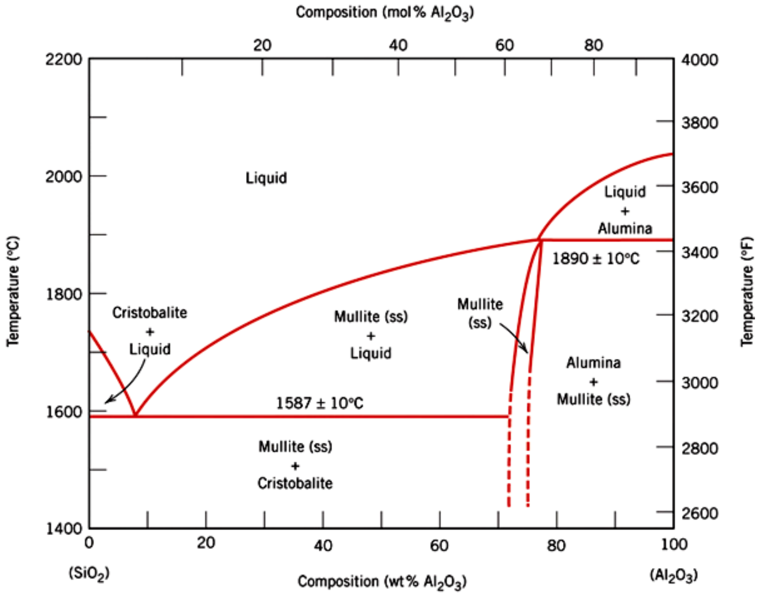

Fig.1. Equilibrium diagram of SiO_2 – Al_2O_3 systems

At the beginning, silico-aluminum refractory products were manufactured based on refractory clays, natural alumina silicates containing a maximum percentage of 38-40% Al_2O_3.

After that, aluminum refractory products with a content of 45-60% Al_2O_3, mullite refractory products with contents of 60-75% Al2O3, mullite-corundum products with 75-90% Al_2O_3 and corundum products with contents of 90-95% Al_2O_3 were made. The followed course was the ennobling of the chamotte obtained from the refractory clays with the additions of technically calcined alumina in increasing proportions with the corresponding modification of the chamoting parameters (temperature, time, etc.) [5-8]. However, in all cases, although the degreaser (chamotte) was increasing in quality, the binder required for shaping remained the same refractory clay, a natural raw material with impurities and which did not allow the increase of Al_2O_3 content in the finished product above a certain limit.

In the years 1960-1970, a new stage of research was undertaken, which aimed the complete elimination of the clay binder and its replacement with hydraulic and chemical binders.

Hydraulic binders (cements) improve the chemical attack stability of the refractory material, but they cause problems in terms of resistance to high temperatures (refractory) due to the melting oxides in the cement, especially if the binder requirement was 10-20%.

Chemical binders had the advantage that their proportion in the shaping mixture did not exceed 5%, so they have a much smaller influence on the composition of the basic refractory material. Initially, as chemical binders, organic binders (natural resins or polymers) were used which bind very well in the cold and in the early stages of the heating process but when burned or in exploitation they were decomposing quickly and lead to the disappearance of the binder properties and as such to the destruction of the product [9,10].

Organic chemical binders, on the other hand, due to their cold binder properties but also due to some reactions they presented in the presence and with the refractory aggregate, ensured a good connection during the entire combustion and exploitation process.

The first used chemical binders were phosphoric acid and its soluble salts (aluminum monophosphate) and sodium silicate. Although they provided good results in production, these binders brought an input of harmful ions to the refractory product $(PO_4)^{3-}$ or $(SiO_4)^{4-}$ which did not allow the production of super aluminous refractory products with over 95% Al_2O_3.

To achieve this goal, the various manufacturing companies have started to manufacture "special binders" consisting of either colloidal binders or various mixtures of inorganic substances to ensure a good bonding of the refractory material but - at the same time a little contamination of the refractory matrix of the product with foreign ions, possibly harmful.

Based on these considerations, the use of colloidal alumina as a binder was established, which, prepared by a special technology, allows the production of refractory products with over 95% Al_2O_3., without bringing melting ions into the refractory mass and so ensuring the possibility of high-quality products.

Regarding the second problem which must be solved, the possibility of shaping products with large dimensions and more products with very complicated shapes or with thin walls, the only suitable shaping technology proved to be the casting from fluid slips.

2. Experimental procedure

Practical achievement of the inert gas injection assembly in liquid steel

2.1. The achievement of the porous plug

Fig. 2 show the complete technological scheme for the manufacture of refractory products with self-hardening binder, including the chemical binder manufacturing technology.

Although the technological scheme shows the manufacturing flow of refractory products cast with self-hardening for the metallurgical industry in the form of a continuous process, it is necessary for the production to take place discontinuously, on batches, this being imposed by the following factors:

- The small amount of hydrated aluminum chloride binder solution does not justify a continuous manufacture, a batch of a few tens of liters of solution reaching for the manufacture of several tons of products. This allows the manufacture of concentrated binder batches at longer periods of time depending on the required production.
- The preparation of the dilute binder solution at a density of 1,040 g / cm^3 must be carried out shortly before the preparation of the pouring paste and only in the strictly necessary quantity for the batch of paste which has to be prepared, to avoid the danger of the onset of precipitation of aluminum hydroxide and thus of the formation of the colloidal binder solution before it is introduced and mixed into the solid material.
- The preparation of the pouring paste must be done in batches that do not exceed the capacity of the available molds, do not exceed in any case its preparation and pouring time (emptying the basin into molds), otherwise there is a danger of coagulation of the paste in the mixer and blocking it.

Of course, these conditions require a good coordination and organization of works so that the best possible labor productivity can be achieved.

Considering that the operations of dosing, preparation of the paste and molding must not exceed 0.5 - 1 hours, taking into account the times of hardening of the paste in the molds and those necessary for stripping and preparing the molds for a new casting, through a good organization of work, depending on the size of the batches manufactured and the number of molds used, up to three castings per shift in the same casting molds can be achieved.

After stripping, the products are kept in the air, on the racks, for 24 hours to continue the curing process and a first phase of slow drying and then are placed in a dryer at a temperature of 1200-1500^{o}C.

Then, after a suitable drying, the products are burned in ovens at temperatures corresponding to the quality of the refractory material used in the preparation of the pasta.

The inert gas injection assembly in the liquid steel from Fig. 3 is composed of:

a- Refractory plug
b- Protective sleeve
c- Safety plate
d- Monoblock support

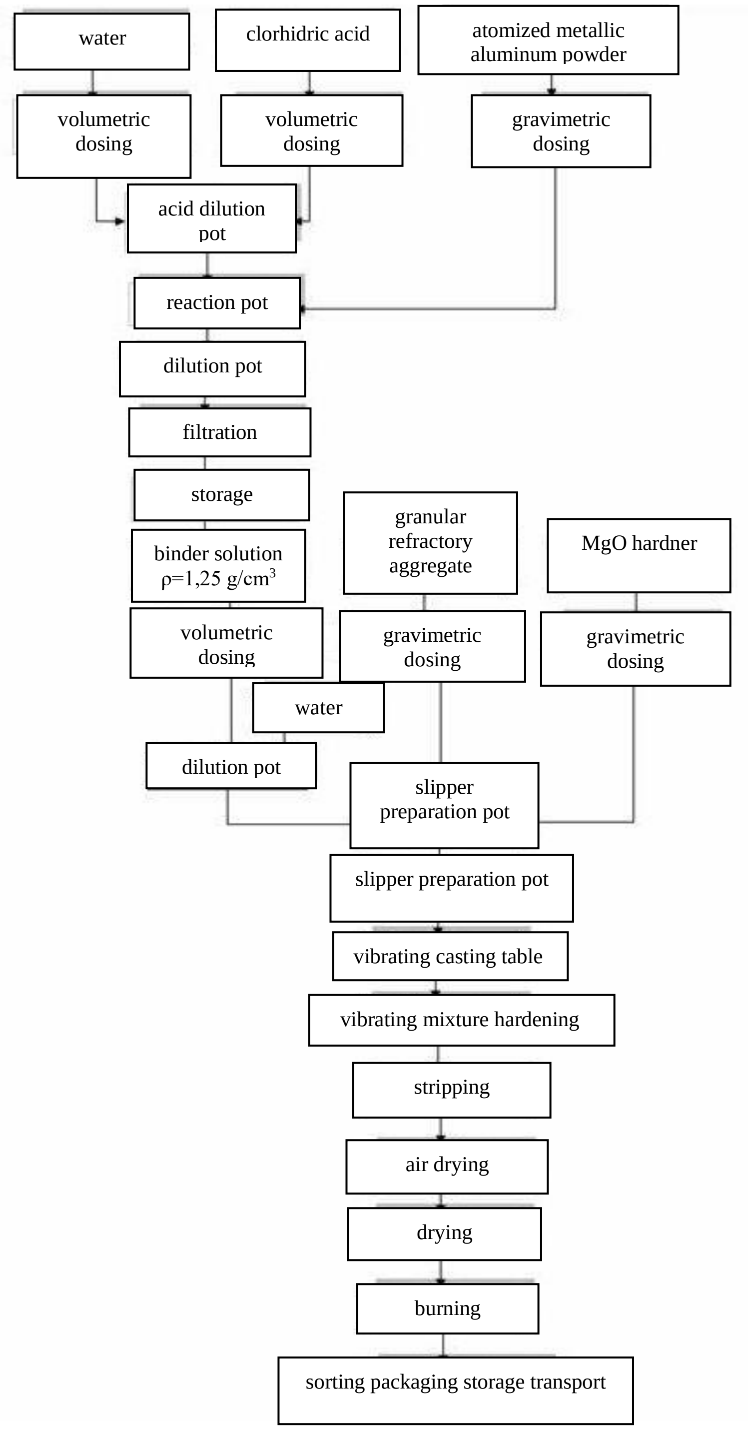

Fig.2. Complete manufacturing scheme of refractory products with self-reinforcing binder [1]

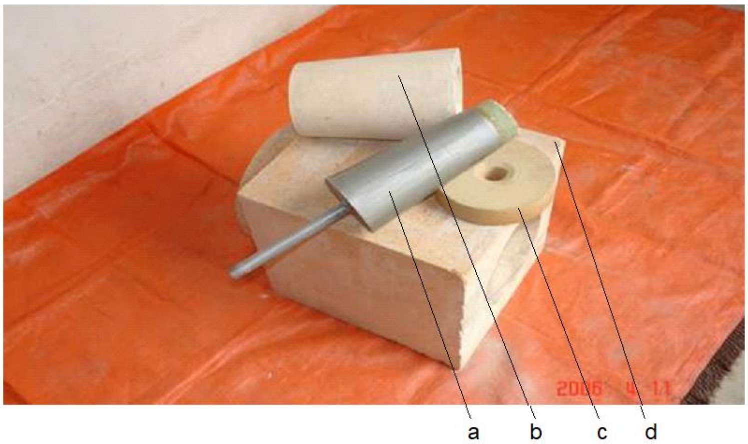

Fig.3. Inert gas injection assembly in liquid steel [1]

Te selection of these products was made on the basis of criteria that took into account the following main factors:

- The parts cannot be manufactured monoblock (in one piece) by the classic technologies practiced in the refractory products factories due to their large dimensions that do not allow molding by pressing because at such elevations it is not possible to achieve a good and uniform compaction of the material (monoblock support).
- In the case of the plug with directed porosity, there is the problem of obtaining the insufflations channels which are made by incorporating some combustible wires which, during the sintering process it is burn leaving channels.
- Also, in the case of a porous plug, it is necessary to obtain a content of over 98% Al_2O_3 which cannot be achieved from refractory masses bound with clayed binders, usually hydraulic.

Raw materials

- high purity commercially tabular alumina (SIKEN Co), with different granulation to obtain a high degree of compaction
- chemical binder
- hardener
- sintering additives

Tabular alumina was analyzed on the ContrAA 300 atomic absorption spectrophotometer, owned by SC CCPPR SA Alba Iulia.

The chemical binder was prepared on the installation within the Microproduction Workshop of SC CCPPR SA Alba Iulia at a density of 1.25 g / cm^3 and was diluted to a density of 1.02 g / cm^3.

The hardener base on magnesium oxide and the sintering additive based on manganese oxide were used in the state in which it was supplied by the supplier.

Tables 1 and 2 shows the partial chemical composition and particle size distribution of SIKEN tabular alumina.

Table 1

Chemical composition of tabular alumina [1]

Chemical properties of tabular alumina SIKEN			Alumina
Composition	Main phase		α - Al_2O_3
	Partial chemical analysis, [wt %]	P.C.	0,13
		Fe_2O_3	0,04
		Al_2O_3	99,65

Table 2

Particle size distribution of tabular alumina [1]

Physical properties of tabular alumina SIKEN				
Granulometric distribution		Particle size 8-14 mesh	Particle size 14-28 mesh	Passing -325 mesh
Particles	Mass remained on sieve 2,5 mm	19%	5%	-
	Mass remained on sieve 1,25 mm	62%	34%	-
	Mass remained on sieve 0,50 mm	2%	27%	-
	Mass remained on sieve 0,50 mm	17%	34%	-
Passing	Mass remained on sieve 0,060 mm	-	-	1%
	Mass passing trough sieve 0,060 mm	-	-	99%
Density [g/cm^3]	3,85			

The recipe from Table 3 was used to prepare the tabular alumina casting paste (slips).

Table 3

The raw material for the casting paste [1]

Components	R1, %
Tabular alumina 8-14 mesh	35
Tabular alumina 14-28 mesh	10
Tabular alumina -325 mesh	55
Diluted binding 1.020 g/cm^3	13.5
Magnesium oxide	0.14
Manganese oxide	2.0

Since tabular alumina does not show water absorption and therefore the preparation of the slip requires a smaller amount of liquid, the amount of diluted binder used was lower.

The pouring mixture was prepared in a 10-liter vessel equipped with a propeller stirrer. The order of preparation operations was as follows:

1. The dilute binder solution was introduced into the shaker vessel.

2. With the start of the stirrer, the fine-grained tabular alumina was introduced, and then the granular alumina was homogenized, approx. 5 min at progressive speed of 200-1000 rpm.

3. After alumina homogenization with the binder, the magnesium oxide and the manganese oxide were added, continuing the mixing for another 3 minutes, until a good homogenization of the casting mass.

4. After stopping the stirrer, the slip was poured into molds the size of a stopper provided with a network of combustible wires to make the insufflations channels. The molds were placed on a vibrating table and filled with the casting slip. Vibration was done throughout the filling of the molds with material and for about 60 seconds after filling.

5. After 80-120 minutes the material has been sufficiently hardened to allow the stripping and handling in good condition of the products which have subsequently undergone drying and sintering operations after which determinations have been made on the chemical and physical-mechanical properties.

2.2. Construction of the protection bush, the safety plate and the one-piece support

The raw materials used are:

- superaluminous chamotte of different granulations to obtain a high degree of compaction
- chemical binder
- reinforcer
- sintering additives

The superaluminous chamotte was analyzed on the ContrAA 300 atomic absorption spectrophotometer, the partial chemical analysis is given in Table 4.

The chemical binder was prepared on the installation within the Microproduction Workshop of SC CCPPR SA Alba Iulia at a density of 1.25 g/cm^3 and was diluted to a density of 1.02 g / cm^3.

The magnesium oxide hardener and the manganese oxide sintering additive were used in the state in which it was supplied.

Table 4

Chemical composition of the superaluminous chamotte [1]

Chemical properties of chamotte SA 68 A			Chamotte SA 68 A
Composition	Main phase		mullite
	Partial chemical analysis, [wt %]	P.C.	0.57
		Fe_2O_3	0.98
		Al_2O_3	70.04

The recipe used to prepare the superaluminous chamotte pouring pasties is shown in table 5.

Table 5

Pouring paste preparation recipe [1]

Components	R1,%
Chamotte fraction 0-3.2 mm	55
Fraction chamotte under 0.06 mm	45
Diluted binding 1.020 g/cm^3	14
Magnesium oxide	0.14
Manganese oxide	2.0

The pouring mixture was prepared in a 10-l vessel with a propeller stirrer. The steps presented previously were followed with the specification that the slip was cast in different molds depending on the desired part.

Drying of molded products

After hardening in molds, which time ranged from tens to 2 hours depending on the shape and size of the cast part (wall thickness, shape, size), preparation conditions and environmental factors, the products were stripped, and they were left to air dry for 24 hours. After that, they were placed in the dryer room at a temperature of 120-1500^{o}C where they were kept for another 8-24 hours.

Burning products

In all cases, the dried products were placed in the oven room 1650^{o}C of S.C. CCPPR S.A. Alba Iulia and were burned after combustion charts according to their Al_2O_3 content. These diagrams are shown in Figs. 4 and 5.

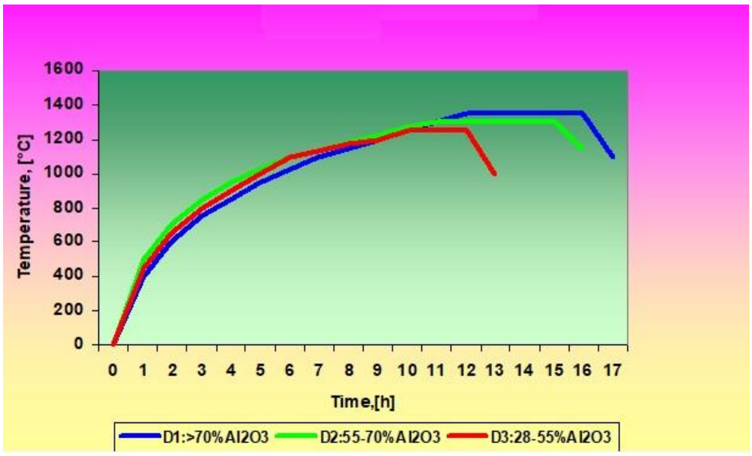

Fig. 4 Porous plug burning diagram

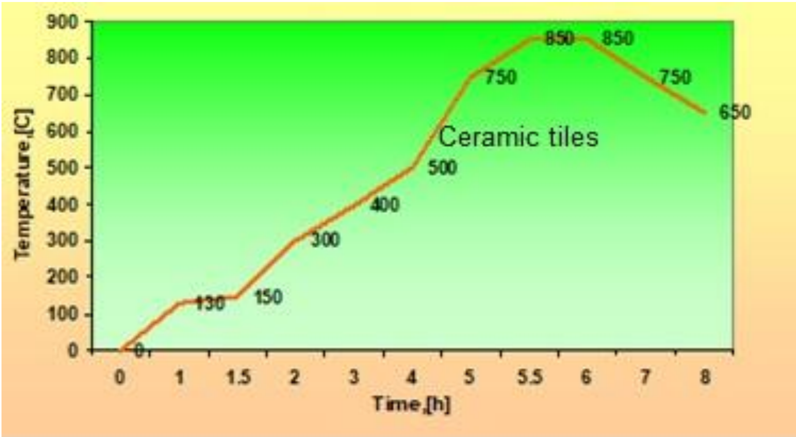

Fig. 5 Diagram of burning bushing, plate and monoblock support

Characterization of manufactured refractory products

When leaving the oven, the samples were subjected to visual examinations in terms of shape deviations (cracks, shards) and then in the laboratory where chemical and physical-mechanical determinations were made. The characteristics of the bubbling assembly are given in Table 6.

Table 6

Characteristics of the components of the bubbling assembly

Characteristics	Plug with directed porosity			Protective sleeve (plug)		
	National recommended	Made in bach	International recommendation	Made in country	Made in batch	International recommendation
Chemical composition Al_2O_3 % Fe_2O_3 %	Min. 98 Max. 1.0	98.0-98.6 0.07-0.12	98 0.5	Min.85.0 Max. 1.0	86.12-87.95 0.58-0.71	Min.85 Max.1.0
Apparent porosity, %	-	29.4-29.8	-	Max.20	22.4-27.9	Max.27
Apparent density, g/cm^3	Min.2.60	2.65-2.79	2,70	Min.2.70	2.53-2.70	Min.2.60
Compression strength, N/mm^2	Min. 20	32.9-33.8	-	Min.15	54-68	Min.50
Refractivity, I.P	192	192	-	192	192	-
Temparature ,ºC	-	-	1.700	-	-	1.700

3.Results and discussions

From the qualitative characteristics determined in the laboratory conditions, the data presented in Table 6 reveals the following aspects: Compared to the products currently manufactured in the country, respectively compared to the norms of imposed quality, the products manufactured by the new technology, show clearly superior characteristics especially in terms of compactness (lower apparent porosity, much higher compressive strength).

- Compared to the imported products, respectively compared to the recommendations of foreign companies, the results obtained are comparable.

Being used in the same place, on the bottom of the steel casting pot, the two refractory parts are subjected, in principle, to the same thermal, chemical, and mechanical stresses.

However, due to the different operating conditions of the casting pot, conditions that differ from one steelworks to another both for objective reasons (capacity of the ladle used, temperature of the steel bath, time of stay of the steel in the pot, type of steel manufactured, the time of gas blowing, etc.), as well as for subjective reasons (how the refractory masonry of the ladle is performed and its current repairs, how the preheating regime of the ladle is observed and - in general - how all technological prescriptions are observed related to human activity), the intensity with which the various aggressive factors act on the refractory material may differ quite a bit from case to case, depending on the specifics of the operating regime as can be seen during the follow-up activities manufactured for testing. From this point of view, it was considered appropriate and necessary to verify their durability under operating conditions for the beneficiaries who agreed to

4. Conclusions

Although the steel pouring ladle was originally designed as a machine for transporting liquid steel from the processing furnace to the casting site, the development of modern steel technologies has transformed it into a processing machine in which alloying operations are carried out, homogenization, etc.

The parts made according to the technology presented in this paper are currently the weak point of refractory masonry due to which the work of the ladle must be interrupted to replace them when wear becomes dangerous and threatens to favor perforations. An increasing in the service life of these parts leads to significant savings in the steel casting process. The cost of a bubbling assembly (porous insufflations plug, protection sleeve, sealing ring and support) currently amounts to approximately 595 euro / set, much lower than the import purchase.

In addition to these direct savings for refractory material, however, several collateral but calculable savings are obtained by:

- prolongation of the cycle (campaign) of exploitation of the pot, so the elimination of the stations for the replacement of the respective parts (including dead times for cooling the pot, restoration of the gas supply assembly and reheating of the ladle to be introduced in the production circuit).

- reducing labor costs to remove worn-out assembly and building new assembly.

- reduction of methane gas costs for reheating the pot.

This opens the possibility of increasing the production of domestic refractory materials, reducing imports, and creating new jobs.

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