EXPERIMENTAL RESEARCH TO OBTAIN A CHEMICAL BINDER USED IN THE MANUFACTURING PROCESS OF REFRACTORY MATERIALS BASED ON ALUMINUM

A. ISTRATE[1], M. BUZDUGA[2], M. CIURDAS[3*]

In this paper, the authors present their own laboratory research to obtain a chemical binder, used in the manufacturing process of alumina-based refractory materials. This binder must not form $Al(OH)_3$ gel to settle before the solution is used as a binder. From the study carried out on the chemical binders used in the refractory industry today, it follows that the most suitable for the manufacture of refractory products are colloid-based inorganic binders. The purpose of the research presented in this paper was to study the possibility of obtaining a chemical binder and to establish its manufacturing technology.

Keywords: refractory materials, silica, alumina, chemical binder, ceramic blocks

1. Introduction

Refractories are materials with a high melting temperature. Conventionally, refractory materials are those that resist, without melting, at temperatures above 1500ºC (in some countries, above 1580ºC). Oxidized refractories have the most important share in production and use. [1-8]. Clay binder is the vulnerable constituent of refractory masses and products. If the aggregates have permanently improved (aluminous - mullite - super aluminous - corundonic fireclays), the binding clays have remained at their natural, non-homogeneous composition, with accompanying minerals and impurities that reduce the thermal characteristics of the refractory product.

Clay minerals are formed by a variable succession, ordered, of groups of sheets with different structures. The following minerals are especially found in refractory clays: kaolinite, halloysite, illite, quartz, montmorillonite. The minerals that accompany and form the clay impurities are calcite, dolomite, pyrite, marcasite, iron oxides, alkalis [1, 9-11].

[1] PhD student, Faculty of Materials Science and Engineering, University POLITEHNICA of Bucharest, Romania, e-mail: bela91bz@yahoo.com
[2] PhD eng., General Manager, S.C. C.C.P.P.R. S.A. Alba Iulia, Alba Iulia, Romania, e-mail: ccppr@rdslink.ro
[3] Lecturer, Faculty of Materials Science and Engineering, University POLITEHNICA of Bucharest, Romania, * corresponding author, e-mail: ciurdasmariana@yahoo.com

Due to the need to completely eliminate these shortcomings, other binders were sought.

Thus, in the first phase, the tendency to use refractory cements appeared.

Aluminous cements - multicomponent binders like Portland cements are usually obtained by grinding the corresponding clinkers resulting, in turn, by burning until sintering, vitrification or melting of mixtures of limestone and bauxite or other raw materials of similar compositions [12-16].

The oxide composition of alumina cements includes as main oxides: CaO, Al_2O_3, SiO_2 and Fe_2O_3; the content in these oxides varies, usually within the following limits: 20 – 40% CaO, 30 – 80% Al_2O_3, 0 – 5% Fe_2O_3, 0 – 5% SiO_2.

Along with the main component oxides, the presence of titanium dioxide, magnesium oxide, alkaline oxides, sulfur (as sulfates) is also noticeable; the content in all these compounds, and especially in the last three, must be strictly limited, to very low values.

When using refractory cements for masses with high refractoriness, it is indicated that subsidiary oxides, such as Fe_2O_3 and SiO_2, should be practically completely absent from the clinker composition. Under these conditions, the alumina clinker compositionally falls into the CaO-Al_2O_3 binary oxide system, the Al_2O_3/CaO molar ratio reaching the maximum value of 2.2 while maintaining a suitable binding behavior.

The mineralogical composition of the alumina clinkers is essentially determined by the oxide composition, as well as by the method of burning (by melting, clinkering or sintering) and cooling them. Thus, if the clinkers obtained by sintering from raw materials containing practically only CaO and Al_2O_3, are devoid of glassy phase, the clinkers obtained by melting, from raw materials with a relatively high content of Fe_2O_3, SiO_2 and subsidiary oxides - considered together, contain up to at 25% vitreous phase.

Monocalcium aluminate is the main mineralogical component of alumina clinkers, giving them a lamellar and fibrous structure.

The compound $12CaO \cdot 7Al_2O_3$ crystallizes in the cubic system. This aluminate takes water from the atmosphere, when it is heated in air, the composition of the formed phase being $Ca_{12}Al_{14}O_{32}(OH)_2$; hydroxylation causes contraction of the elementary cell. Hydration of the compound increases its stability under normal conditions, due to a higher order of the atomic arrangement.

Monocalcium dialuminate is presented in the form of large, acicular, monoclinic, strongly birefringent crystals.

Later, chemical binders appeared which brought the great advantage of being used only in very small percentages compared to ceramic (clay) or cement binders.

If clay and/or cement binders require a percentage of 10-20% of the refractory mass, with all the improvements in manufacturing technologies, chemical binders bind the degreaser matrix (aggregate) even at additions of only 5-10% or even less.

Unfortunately, these binders also present a series of disadvantages in the shaping of refractory product masses. Thus, in the context of the classic pressing (for shaped products) or printing (for non-shaped refractory materials) technologies, the disadvantage is from the point of view of putting into operation (bonding to molds, stamping hammers, etc.) and of the resistances in the state raw of the products. On the other hand, the burning of the raw product can be done much faster because, after a heat treatment at 120-200°C, the masses no longer suffer losses or transformations that lead to considerable volume variations [1, 11-14].

The first chemical binders used were phosphoric acid and its soluble salts (aluminum monophosphate) and sodium silicate. Although they gave good results in production, these binders brought an intake of harmful ions to the refractory product $(PO_4)_3$-or $(SiO_4)_4$ - which did not allow the realization of superaluminous refractory products with over 95% Al_2O_3 [1].

Sintering at lower temperatures can be achieved by using alumina with a high degree of dispersion, as well as by adding mineralizers such as: TiO_2, MnO_2, Cu_2O, GeO_2, Fe_2O_3, CaO, MgO, BaO, Cr_2O_3, etc. [2-4, 17-19].

These mineralizers allow densification by recrystallization, with or without the presence of the liquid phase [19-22].

The objective of the research presented in this work was to define a technology for the manufacture of the chemical binder, aluminum chloride, used in the manufacture of high-quality refractory products.

2. Materials and methods

2.1. The raw materials used to make a chemical binder

To obtain an acidic aluminum chloride solution, the reaction between HCl and metallic Al was used.

By dissolving metallic aluminum in hydrochloric acid solution, a solution of aluminum chloride is obtained with a pH between 1.5-2.0, much below the precipitation range of aluminum hydroxide.

Hydrochloric acid from S.C.UTCHIM S.R.L Râmnicu-Vâlcea was used with a minimum content of 32.5% HCl and no free chlorine with the characteristics shown in table 1.

Table 1

Characteristics of hydrochloric acid used in the preparation of the chemical binder

Characteristic	UM	Real values	Normal values	Test method
Appearance		Clear liquid		Standard 339-80

Color		Colorless to greenish yellow		Standard 339-80
HCl content	%	32.5	32	Standard 339-80
Iron	%	0.0014	0.005	Standard 339-80
SO_2	%	0.0091	0.05	Standard 339-80
Warranty period	months	6	6	Standard 339-80

Atomized aluminum powder type AA 300 is procured from S.C. ALBA ALUMINIU S.R.L. Zlatna and has the characteristics presented in table 2.

Table 2

Characteristics of atomized aluminum powder

Technical specifications	Standard	UM	Value	
			Estimated	**Realized**
0.300 mm sieve remains	SR ISO 24497	%	Max.2	1,012
Active aluminum content		%	97,5	97,5

2.2. The working method used to make a chemical binder

Aluminum powder was added to 500 ml of hydrochloric acid diluted with 1 l of water. Although initially the reaction is difficult to initiate, once started it proceeds very violently, being strongly exothermic.

For this reason, the aluminum powder was introduced gradually, in small portions, waiting each time for the end of the dissolution of the amount of aluminum powder, previously added, indicated by the effervescence stopping. Aluminum powder was thus added until saturation, when the reaction no longer takes place.

With the amount of hydrochloric acid solution indicated above, 116 g of aluminum powder were consumed, obtaining approx. 1.3 l concentrated $AlCl_3$ solution with a density of 1.24 g/cm^3. A part of this solution was stored in closed glass vessels, in order to verify the possibility of keeping it without essential changes. The other part was used to make cast aluminum tabular specimens. Tabular alumina and a diluted binder solution consisting of aluminum chloride binder and water in a ratio of 1:5 were used to obtain the casting slurry. Although diluting the chloride solution changes the pH towards the neutral gelation range, the process is too slow and curing takes a long time. This led to the need to add a "hardener" to the slurry to accelerate the hardening process by forming the aluminum hydroxide gel.

3. Laboratory research to establish the technology of obtaining a chemical binder

3.1. Research to identify a suitable material as a reinforcement

To regulate the coagulation time of the casting mass in the molds, pH modifiers were used to bring the binder solution to a pH above 4, the range in which the hydrated alumina gel is obtained. Ammonium hydroxide was used for this purpose, with the idea of not changing the Al_2O_3 content of the mass.

However, the reaction proved to be too strong and the hardening takes place quickly, still in the vessel for preparing the slip without allowing it to be poured into molds.

Also with the idea of not contaminating the material with foreign ions, gelation was tried by adding aluminum powder. In this case, however, the process takes place very slowly. Finally, the addition of small amounts of magnesium oxide (MgO) of 0.15% relative to the solid material in the slip was resorted to.

This addition led to satisfactory results, the paste hardening after 1h 30' to 2 h of preparation (from the moment of adding the hardener), sufficient time for a good homogenization of the components and filling of the molds.

Once these things were established, we moved on to the creation of some products in the laboratory and their characterization.

The replacement of the clay binder with a chemical binder that allows the self-hardening of the casting paste in molds makes it possible for the finished products obtained to present higher Al_2O_3 contents, respectively lower Fe_2O_3 and other fusible oxide contents compared to similar classic products, thus conferring properties thermomechanical and thermochemical superior to the latter.

The chemical binder was chosen in such a way as to increase the Al_2O_3 content of the product by creating, during the burning process, corundum bonds between the solid material particles that form the product matrix.

It has been proven that the chemical binder used can be used both for refractory products based on fireclay and products manufactured based on pure tabular alumina raw materials, which is particularly important in the latter case.

3.2. Establishing the manufacturing technological parameters of the chemical binder

In order to carry out the tests at the laboratory level, we started from raw materials that can currently be obtained at the industrial level and therefore that will be able to be used later in the current production.

In this sense, hydrochloric acid from S.C.UTCHIM S.R.L Râmnicu-Vâlcea was used with a minimum content of 32.5% HCl and without free chlorine with the characteristics in table 1.

The aluminum powder used was purchased from S.C. ALBA ALUMINU S.R.L. Zlatna, type PA 300 (atomized powder) with the characteristics in table 2, with a granulometric analysis of: 315 μm -0.016%, 200 μm-29.816%, 100 μm-69.379%.

Aluminum hydroxide in colloidal form, represents the chemical binder that contributes Al_2O_3 in the process of forming the binder phase in the finished product, it must be characterized mainly by the content of solid substance (Al_2O_3) in the composition.

The specialized literature indicates an optimal content of 8-10% oxide component in the alumina soil used as a binder, soil known as "colloidal alumina".

In order to obtain the colloidal alumina binder, we started from the aluminum chloride produced from the raw materials mentioned above (technical hydrochloric acid and atomized metallic aluminum powder) in aqueous solution.

The aluminum chloride that is formed hydrolyzes in water, the solution presenting an acidic character with a pH below 3, which prevents the hydroxide from gelling.

Aluminum hydroxide solution dissociates as follows:

$$Al^{3+} + 3(OH) \Leftrightarrow Al(OH)_3 \equiv Al(OH)_3 + 3H_2O \Leftrightarrow [Al(OH)_4 \cdot (H_2O)_2]^- + H^+ \quad (1)$$

where, in an acidic environment (with a pH below 4), Al^{3+} or $[Al(O2H)6]^{3+}$ ions predominate, and in a basic environment (above pH 12) complex ions of $[Al(OH)4 \cdot (H2O\ )]^{2-;}$ $[Al(HO)5 \cdot H2O]^{2-}$ or $[Al(OH)6]^{3-}$. Between a pH of 4 and 11.5-12 aluminum hydroxide is insoluble forming aluminum soil (colloidal alumina).

How, following the thermal treatments to which the products are subjected (drying, burning, sintering), Al3+ ions, respectively [Al(H2O)6]3+ transform into the form - Al_2O_3 (the desired form of corundum) and the ions obtained in a basic environment transforms into forms of -Al_2O_3 (beyerite) it was chosen to work in an acidic environment.

Thus, in the first stage, aluminum chloride was formed and hydrolyzed according to the reaction:

$$3HCl + Al + 3H_2O \Leftrightarrow Al(OH)_3 + 3HCl \quad (2)$$

Depending on the concentration, a solution with a pH of 2.0-2.6 is obtained. This pH must not be exceeded in order not to pass into the area where $Al(OH)_3$ is not soluble and is deposited.

A hydrated aluminum chloride solution was prepared as follows:

In a vessel, 1 liter of hydrochloric acid was diluted with 2 liters of water and then 232 grams of aluminum powder were added to form aluminum chloride. The aluminum powder was added in small amounts of 70 grams each, waiting - each time - for the end of the reaction (effervescence) produced by the amount of aluminum added previously. It was decided to manufacture the aluminum chloride solution from more diluted hydrochloric acid in order to avoid the strongly exothermic reaction that produces a sudden volatilization of the water, the released vapors entraining a part of the aluminum powder that is thus lost.

The attempt to hydrate concentrated aluminum chloride with water produced a phenomenon of releasing a dense white mist until a layer of hydrated aluminum chloride forms on the surface, at which point the violent reaction to new additions of the water.

After this moment, new quantities of water can be introduced into the vessel, the hydrolysis proceeding under the same energetic conditions (exothermic), but the relatively large mass of existing water prevents effervescence and the formation of vapors. In order to avoid these undesirable phenomena from the beginning of the reaction of aluminum chloride formation and its hydrolysis, it was resorted to starting the reaction with diluted hydrochloric acid from the beginning. However, the strongly exothermic reaction raises the temperature of the solution to 85-900^{o}C.

The progress of the reaction can also be followed by controlling the temperature. An optimal reaction speed is obtained at temperatures around 600^{o}C. At lower temperatures the reaction proceeds more slowly requiring longer hydrolysis times, and at temperatures above 70-800^{o} C the reaction is so intense that it produces a strong "boiling" of the solution due to the release of hydrogen, this effervescence can produce entrainment (loss) of aluminum powder or a spill of the solution over the edges of the vessel. Through the process shown, from 1 liter of HCl diluted with 2 liters of water and 232 grams of aluminum powder, after the completion of the reaction and the cooling of the solution, a quantity of 2.6 liters of hydrated aluminum chloride solution with a density of 1.25 g/ cm^3 and a pH of 2.5. This solution has a content of approx. 13.3% Al_2O_3 according to the graph shown in Fig. 1 which shows the variation of the concentration in the oxide compound with the density of the solution.

To verify this Al_2O_3 content, determined with an immersion densitometer, a determination was made by dry evaporation of a quantity of solution and calcination of the residue at 1000^{o}C, the result obtained was 13.5% Al_2O_3 (gravimetric), which indicates a sufficiently accurate assessment of the Al_2O_3 content based on immersion densitometer measurements, much simpler and faster in the practice of quality control in production.

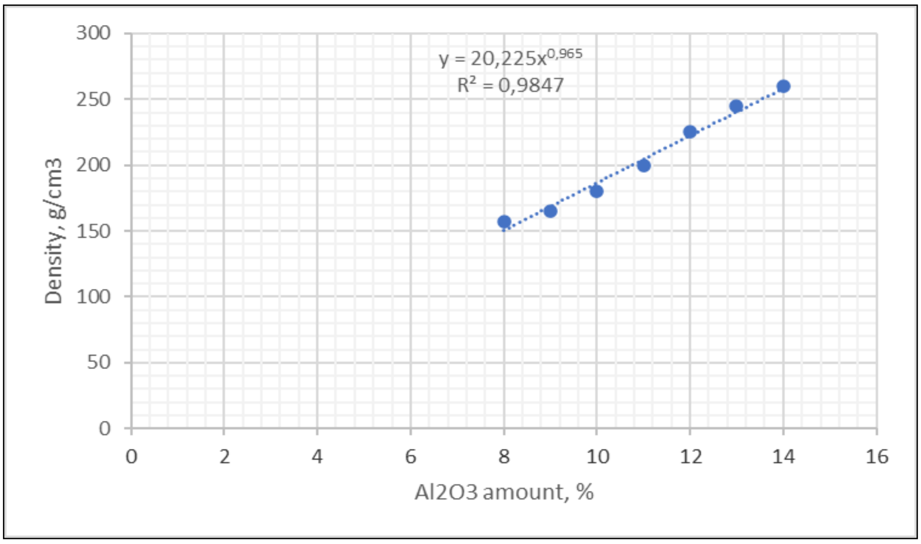

Fig. 1. The variation of the density of the chemical binder with the Al_2O_3 amount

This solution can be kept in good conditions for a long time in closed vessels in order not to change its pH because it is in the pH range below 4 there is no danger of the deposition of aluminum hydroxide which is insoluble only between pH = 4 - 12.

Moreover, the solution samples kept in the laboratory from the first phase of the works showed no traces of deposition after more than three months of storage.

3.3. Description of the manufacturing technology of the chemical binder

The manufacturing flow of the chemical binder includes the following stages:

Reception of raw materials

For the manufacture of the self-reinforcing binder based on hydrated aluminum chloride, the following basic raw materials are used:

Technical hydrochloric acid. In the laboratory tests, a hydrochloric acid with a content of 32.5% HCl and without free chlorine was used, purchased from SC UTCHIM SRL Râmnicu Vâlcea.

It is mentioned that any kind of hydrochloric acid can be used, with different concentrations, provided that it does not contain impurities in a quantity greater than 0.001%.

Depending on the concentration of the purchased hydrochloric acid solution, an appropriate dosage will be made to obtain the desired binder.

Atomized aluminum powder type PA 300 procured from S.C. ALBA ALUMINIU S.R.L. Zlatna, at grain size below 0.315 mm.

Preparation of raw materials

These raw materials do not require additional training by the user, as they are used as such in the technological process of manufacturing the binder.

Dosage of raw materials

To obtain hydrated aluminum chloride, the manufacturing recipes shown in table 3 are used.

Table 3

Manufacturing recipe of a self-reinforcing chemical binder

Compound	Chemical binder
HCl (calculated volumetrically in HCl 100%), %	85
Al metallic (calculated gravimetrically)	15

Although in accordance with the theoretical reaction:

$$3HCl + Al \rightarrow AlCl_3 + 3H+ \quad (3)$$

the gravimetric proportions of HCl and Al would be 80% : 20%, due to the variable density of the HCl solution on the one hand and the incomplete reaction on the other, the amounts of components differ slightly. For these reasons, it is recommended that before the start of manufacturing, a laboratory sample is made to indicate the proportion of the two components in order to obtain a saturated solution.

For this, in 100 ml of HCl (at the concentration and characteristics procured), quantities of aluminum powder will be gradually dissolved until the complete cessation of the reaction (ceasing of effervescence), but without obtaining an unreacted alumina residue. Based on this sample, the proportion of HCl and Al will be established for each batch of raw materials purchased.

Preparation of the solution

In a plastic container (or an enameled or corrosion-protected metal container) put the hydrochloric acid and water to obtain a solution of hydrochloric acid diluted to 10-15%.

This is necessary to avoid a too strong reaction and the formation of an effervescence that will lead to a sudden increase in temperature and gas releases that will carry quantities of aluminum powder.

Metallic aluminum is gradually added to this solution in small amounts that do not exceed 6-7% of the total amount of aluminum required for the reaction.

After approx. 5 minute is necessary to initiate the reaction, a strong effervescence with hydrogen release and an increase in temperature is observed.

In the next 15-20 minutes, the complete dissolution of the first amount of metal takes place, after which the effervescence disappears and the second portion can be added.

This time the reaction starts immediately because the temperature of the solution is optimal for its development under normal conditions.

Table 4 shows the reaction intensities depending on the temperature of the solution.

Table 4

Kinetics of the reaction to obtain the binder as a function of temperature

25°C	very slow, imperceptible reaction
50°C	slow reaction with moderate effervescence
70°C	strong reaction with effervescence throughout the mass
80-90°C	very strong reaction with formation of foam on the surface of the solution and tendency to spill

It should be noted that it is not considered necessary for the reaction vessel to have a heating system for priming the reaction and regulating the optimal reaction temperature because, as shown, after a not too long time the reaction is also primed in the cold and its exothermic effect heats the solution at a temperature high enough for its continuation.

In extreme situations, when the temperature rises too much, the intensity of the reaction can be suddenly reduced by adding a quantity of cold water which, however, must not exceed 1/10 of the mass of the mixture. The portions of aluminum powder are added in this way, each time waiting for the end of the effervescence of the reaction from the previous portion, until the complete consumption of the amount of aluminum powder. For a mixture of 20 liter of solution, the method of adding portions of aluminum powder, the method of application, as well as the time interval required for the reaction until the effervescence disappears are shown in table 5.

Table 5

Temporal stages of obtaining the binder

Sample	**Amount grams**	**Method of application**	**Reaction time, minutes**	**Temperature, °C**
Beginning of the reaction				25
P 1	85 g	The whole quantity	after 15 min the reaction is initiated 5 min intense reaction	50 75
P 2	85 g	Add the quantity little by little with continuous stirring	10 min intense reaction	80
P 3	85 g	Add the quantity little by little with continuous stirring	8 min intense reaction	85
P 4	85 g	Add the quantity little by little with continuous stirring	7 min intense reaction	85
P 5	85 g	Add the quantity little by little with continuous stirring	8 min intense reaction	85

P 6	85 g	Add the quantity little by little with continuous stirring	7 min intense reaction	85
P 7	85 g	Add the quantity little by little with continuous stirring	5 min intense reaction	90
P 8	85 g	Add the entire amount	5 min intense reaction	90
P 9	85 g	Add the entire amount	5 min intense reaction	90
P 10	85 g	Add the entire amount	5 min intense reaction	90
P 11	85 g	Add the entire amount	5 min intense reaction	90
P 12	85 g	Add the entire amount	5 min intense reaction	90
P13	85 g	Add the entire amount	5 min intense reaction	90
P 14	85 g	Add the entire amount	5 min intense reaction	90
Total reaction time			100 min	

The variation of the working temperature in the experimental samples is presented in Fig. 2. The amount of Al_2O_3 in each of the samples was 85 grams.

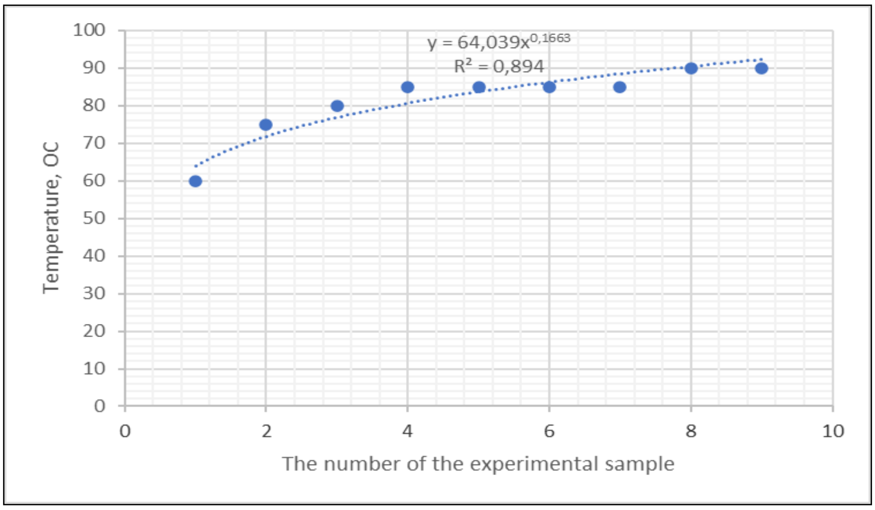

Fig. 2. The variation of the working temperature in the experimental samples

The entire process can be followed visually and does not require measuring and control equipment. After finishing the process of dissolving metallic aluminum, leave the solution in the vessel for 24 hours to cool it down to the ambient temperature. After cooling, the solution is transferred to a dilution vessel also made of anti-acid or suitably protected material and density samples are taken. Depending on the obtained density, water is added until a final density of 1.24 g/cm^3 is obtained. The hydrated aluminum chloride solution prepared in this way is stored in closed antacid containers and can be used as such in the preparation of casting pastes. The shelf life of the solution seems to be unlimited; laboratory tests proving that for three months there were no changes in the composition or in its mode of action in use.

Manufacturing control

The control of the manufacturing of the binder solution consists only in measuring the density following the reaction process, after its cooling, and the control of the dilution process also through density measurements.

Optionally, especially when manufacturing the first batches, a control of the pH of the final stored solution can be introduced immediately after completion and then periodically at different time intervals.

The sequence of operations required for the manufacture of the chemical binder and the technological flow of the manufacture of the chemical binder are shown in Figs. 3 and 4.

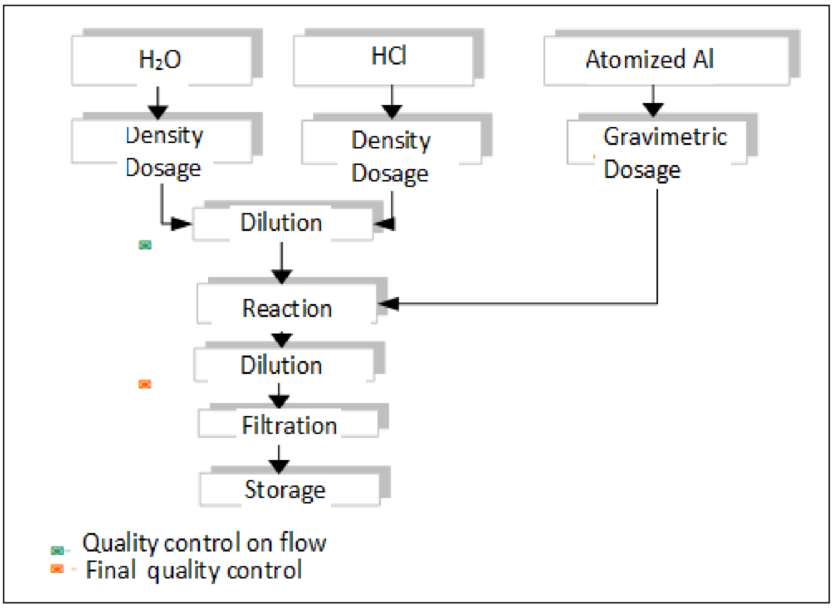

Fig.3. The sequence of operations required to manufacture the chemical binder [1]

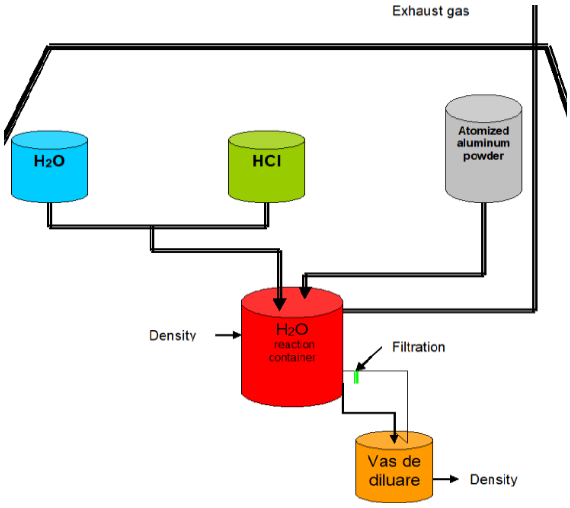

Fig. 4. Technological flow of chemical binder manufacturing - principle diagram [1]

After finalizing the manufacturing technology of the chemical binder, an installation for obtaining this type of binder was created within the Microproduction Workshop at SC CCPPR SA Alba Iulia.

The installation consists of:

- Vessel for storage and dilution of the obtained chemical binder solution with a capacity of 30 liters. The vessel is made of anti-acid material - polyester resin reinforced with glass fiber and is equipped with a lid and tap for dosing the binder.

- Reaction vessel with a capacity of 80 liters. The vessel is made of antacid polyester resin material reinforced with glass fiber and is equipped with a lid, an exhaust system for the resulting reaction gases, a strainer and a discharge system in the storage vessel.

- **Potable** water storage vessel made of plastic material. Hydrochloric acid storage vessel is made of plastic material. The atomized aluminum powder storage vessel is made of plastic material.

4. Discussions and conclusions

Refractory products, regardless of whether they are shaped products (with precise shapes and sizes) or unshaped products, in bulk (mortars, concretes, molding materials, casting materials, refractory putties, etc.) are composed of two basic components, the refractory aggregate (degreaser), the main component that generally represents more than 70% of the material's composition and forms the structure of the product and the binder that binds the aggregate into a monolith.

Refractory products manufactured in the country at this moment with clay binders reach a maximum of 90-92% Al_2O_3, the remaining 8-10% representing impurities of the refractory product by foreign ions that come especially from the clay binder introduced in the refractory mass.

The creation of a new type of binder starting from aluminum powders in conditions of maximum economic efficiency and in conditions of advanced environmental protection would determine the possibility of making refractory products in the country, compatible with similar products from other developed countries of the world. This would allow the Romanian refractory industry to reach the standards of the European Union, a priority objective of Romania's industrial policy for the coming years.

The direct result of the research presented in this paper consists in obtaining a chemical binder and studying the influence of some additives on aluminum refractories in order to obtain special refractory products with superior characteristics used in industry, studying the expansion of the field of use of these products. The applied, subsequent value of the research is given by the possibility of developing technologies for obtaining both the chemical binder and the refractory products manufactured with this binder and their use in the metallurgical, chemical, machine building, ceramic, refractories, glass, etc. .

The possibility of obtaining superior refractory products that can be used in severe operating conditions, high temperatures or corrosive environments is considered.

Acknowledgments:

This work was supported by Human Capital Operational Program, Priority Axis 6— Education and skills, Project: Training of doctoral students and postdoctoral researchers in order to acquire applied research skills—SMART Cod MySMIS: 153734, and the authors would want to thank University “Politechnica” of Bucharest for the chance to publish this paper.

R E F E R E N C E S

[1] Miron Dorică BUZDUGA, Utilizarea raţionala a produselor refractare speciale, obţinute prin tehnologii neconvenţionale in industrie, Teză de doctorat, Bucureşti 2010

[2] Goleanu, M. Buzduga, N. Constantin, A. Comsa, M.Butu, Effects of Additives on the Sintering Process of Al2O3-based Ceramic Materials 2 th International Congress on Ceramics, Verona, 29 iun-4 iul 2008-3-Pag. 38-45

[3] Teoreanu; N.Ciocea, Tehnologia produselor ceramice şi refractare vol.I - II-Ed.Tehnică Bucureşti 1985

[4] P. Tofel., Evaluation of properties of newly developed refractory materials produced in SEEIF ceramic, a.s.., Interceram – Int. Ceram. Rev., 65 (2016), pp. 8-11;

[5] E M Vlad, V E Caloian, C Pandelescu, E F Plopeanu, V Oancea, V Rucai, N Constantin and M Hritac, Experimental research on the effect of additives on the sintering process of alumina-based refractory materials, Conferinta Internationala, InternationalConference on Applied

Sciences – ICAS 2020, May 22, 2020, Hunedoara, Romania, indexata ISI, http://icas.science/forms/Program_ICAS2020

[6] S.E. Kalakhi, A. Samdi, R. Moussa, M. Gomina., Production of corundum-mullite mixture with high added value from raw materials of Morocco., New J. Glas. Ceram., 06 (2016), pp. 9-14;

[7] A. Manni, A. Elhaddar, A. El Bouari, I.-E. El Amrani El Hassani, C. Sadik., Complete characterization of Berrechid clays (Morocco) and manufacturing of new ceramic using minimal amounts of feldspars: economic implication, Case Stud. Constr. Mater., 7 (2017), pp. 144-153

[8] Jorge López-Cuevas, Claudia Magdalena López-Badillo, Juan Méndez-Nonell; Synthesis and phase evolution of a glass-ceramic biomaterial with near-eutectic composition of the pseudo-binary system diopside–tricalcium phosphate, Bol Soc Esp Ceram Vidr. 2021;60:74-82;

[9] Radu BUZDUGA, Nicolae Constantin, Aurica Goleanu: Research on the synthesis of cordierite in refractory masses, UNIVERSITY POLITEHNICA OF BUCHAREST SCIENTIFIC BULLETIN SERIES B - CHEMISTRY AND MATERIALS SCIENCE Volume 78, Pages: 230-236 Issue 1, Published: 2016 - ISSN 1454-2331, WOS:000417051900023.

[10] A. Istrate, M. D. Buzduga, B. Florea, M. Ciurdaș, R. M. Iordăchescu, Experimental research for the production of casting refractory materials with chemical binding, U.P.B. Sci. Bull., Series B, Vol. 84, Iss. 3, 2022 ISSN 1454-2331

[11] Valeriu Rucai, Nicolae Constantin, Cristian Dobrescu, Experimental research program regarding the influence of thermo-time treatment of multicomponent ni-base melting on their properties in solid phase, U.P.B. Sci. Bull., Series B, Vol. 77, Iss. 4, 2015 ISSN 1454-2331, pag.359-364

[12] Ardelean, E (Ardelean, Erika) ; Socalici, A (Socalici, Ana) ; Lupu, O (Lupu, Oana) ; Bistrian, D (Bistrian, Diana); Dobrescu, C (Dobrescu, Cristian ; Constantin, N (Constantin, Nicolae), Recovery of Waste with a High Iron Content in the Context of the Circular Economy, MATERIALS, Volume 15, Issue 14, Article Number 4995, DOI 10.3390/ma15144995, Published JUL 2022, Indexed 2022-08-04, Accession Number WOS:000831547900001, PubMed ID 35888462, eISSN 1996-1944,

[13] N. Constantin, I. Butnariu, R. Buzduga, C. Dobrescu, M. Buzduga, Establishing the Optimum Composition of Superaluminous Refractory Products, Used for Steel Ladle Bubbling, Revista de Chimie, vol.69, nr.8, 2018, pag 2177-2182, ISSN 0034-7752

[14] Radu BUZDUGA, Nicolae Constantin, Alexandra Lazar: Research on uses plant ashes in processing powders for classical moulding of steel. INTERNATIONAL CONFERENCE ON APPLIED SCIENCES (ICAS2014). Book Series: IOP Conference Series-Materials Science and Engineering Volume 85(2015)012008, Published: 2015, doi:10.1088/1757-899X/85/1/012008 WOS:000357864400008

[15] Radu BUZDUGA, Nicolae Constantin, Adrian Ioana: Solutions to reduce the environmental pollution by the producers of refractories. UNIVERSITY POLITEHNICA OF BUCHAREST SCIENTIFIC BULLETIN SERIES B - CHEMISTRY AND MATERIALS SCIENCE Volume: 80 Issue: 1 Pages: 231-244 Published: 2018, WOS:000428112600019.

[16] Radu BUZDUGA, Nicolae Constantin, Alexandra Lazar, Adriana Comsa: Research in order to obtain special monolithic refractory material. INTERNATIONAL CONFERENCE COMAT 2014, ROMANIAN ACADEMY OF TECHNICAL SCIENCES „TRANSILVANIA" UNIVERSITY OF BRAŞOV Department of MECHANICS. Book Series: TRANSILVANIA UNIVERSITY PRESS OF BRAŞOV, Published: 2014.

[17] Radu BUZDUGA, Alexandra Lazar Constantin Nicolae: Comparative analysis of technlogical options for the aggregate of blowing inert gases into the steel ladle, produced and used in

Romania; Annals of Faculty Engineering Hunedoara – International Journal of Engineering, Tome XIII [2015] – Fascicule 3 [August]; ISSN: 1584-2673 [CD-Rom; online], ‚Annals-Journal of Engineering, in INDEX COPERNICUS – JOURNAL MASTER LIST, ProQuest database, Google Scholar, http://annals.fih.upt.ro/pdf/AE-AM-40th-2010-full.pdf, BDI.

[18] Teodor Heput, Ana Socalici, Erika Ardelean, Marius Ardelean, Nicolae Constantin, Miron Buzduga, Radu BUZDUGA: Tubular briquette produced from pulverous and small ferrous wastes. UGAL INVENT The first event supporting innovation promoted by "Dunarea de Jos" University of Galati Galați, România, 8 – 10 October 2014, http://www.polmedgreen.ro/UgalINVENT_2014.

[19] E M Vlad, V E Caloian, C Pandelescu, E F Plopeanu, V Oancea, V Rucai, N Constantin and M Hritac, Experimental research on the effect of additives on the sintering process of alumina-based refractory materials, Conferinta Internationala, InternationalConference on Applied Sciences – ICAS 2020, May 22, 2020, Hunedoara, Romania, indexata ISI, http://icas.science/forms/Program_ICAS2020.pdf

[20] L Zgripcea, A Socalici, V Putan1 and C Birtok Băneasă, Unconventional method of cutting aluminum plates using fiber laser with oxygen assist gas, Published under licence by IOP Publishing Ltd Journal of Physics: Conference Series, Volume 2212, International Conference on Applied Sciences (ICAS 2021) 12/05/2021 - 14/05/2021 Online Citation L Zgripcea et al 2022 J. Phys.: Conf. Ser. 2212 012033 DOI 10.1088/1742-6596/2212/1/012033