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RESEARCH IN ORDER TO OBTAIN SPECIAL MONOLITHIC REFRACTORY MATERIALS

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Abstract: *This work aims to bring research of monolithic fire brick products, the main characteristics of LCC (concrete with medium content of cement) and ULCC (concrete with very reduced content of cement) concretes, as well as the influence of certain additives on these characteristics and the advantages of using these concretes in metallurgy. The experimental studies were focused to establish appropriate compositional fields of composite refractory products made from superior materials, judiciously chosen taking into account the operating conditions, to highlight the superior industrial refuse, design and planning flows environmentally friendly technology. The products to be studied in this work will be refractories with different contents of* Al_2O_3 *and* SIO_2*. These products are widely used in metallurgy industry, glass, ceramics, and mechanical engineering.*

Keywords: *monolithic, concrete, fire brick*

1. INTRODUCTION

Classification of refractory concretes according to **ISO/DIS 1927-1:2008** is as follows:

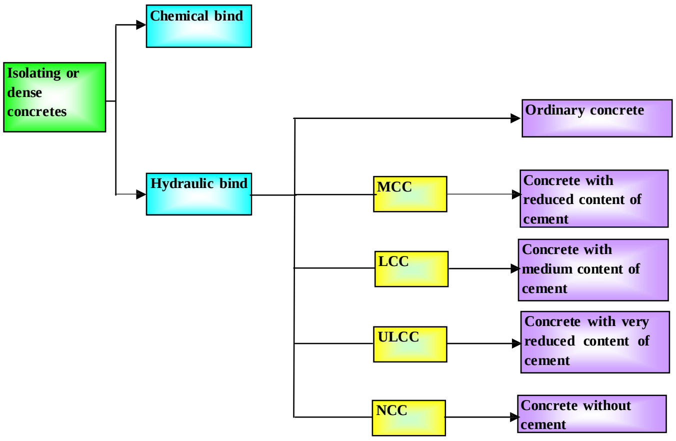

Figure 1: Classification of refractory cements according to **ISO/DIS 1927-1:2008**

Concluding the above, the content of cement in these concretes is:

Conventional concrete	10 – 25 %
Average cement concrete	8 – 15 %
Concrete with low cement	4 – 6 %
Concrete with very low cement	2 – 2,5 %
Concrete without cement	0 %

Figure 2: Classification of refractory concretes according to **ISO/DIS 1927-1:2008**

2. CONCRETES WITH LOW AND VERY LOW CONTENT OF CEMENT

In Romania, although the low cement concretes have been studied even since 1980, those have not been used in mass production. That is due to the fact that low cement concretes are more demanding and sensitive on first heating.

The production of low cement refractory concretes is based upon the use of additives with advanced grinding gauge, due to the fact that in a casting mix, the density obtained with a classic granulometric distribution is limited to the hollows between the grains, which are filled with excess water during processing.[1]

In fig. 3 there is a graphic representation of the dependency of calcium oxide of the cement content, both for an ordinary concrete, and for a reduced cement one.

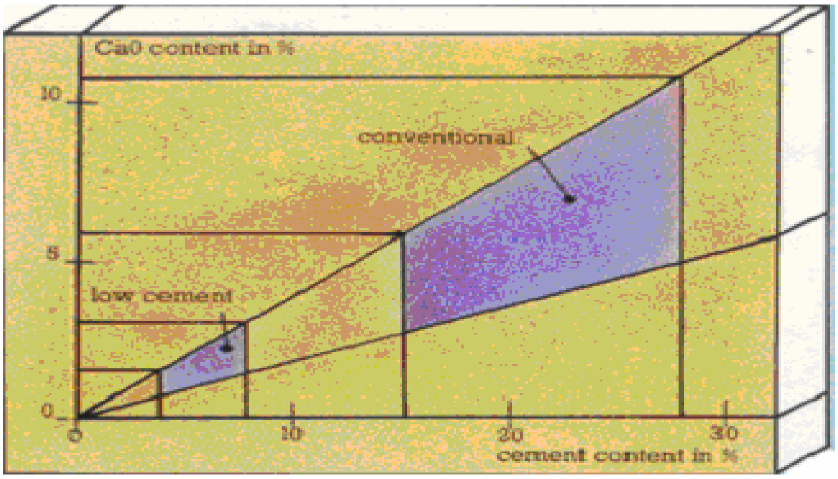

Figure 3: Dependency of CaO on the cement content

In fig. 4 there is a graphic representation of the compression resistance on the temperature. As it can be well seen, for an intermediate temperature (800 - 1000°C) the mechanical resistance of ordinary concretes is much lower than that of low cement concretes.

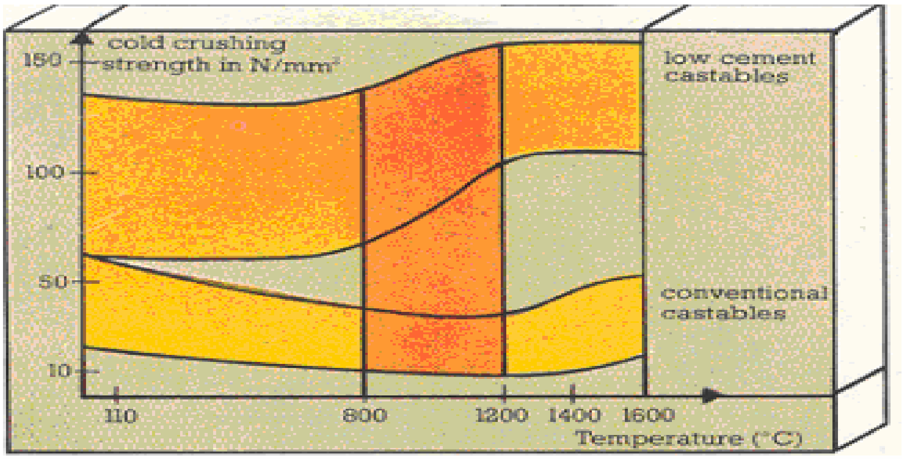

Figure 4: Dependency of mechanical resistance on the temperature

The main feature that isolates concretes with low and very low content of hydraulic binder from other types of cement is the presence of very fine components. This very fine material replaces part of the cement content in the conventional concrete.[1]

In table 1 we present the influence of LCC concrete properties varying with its components.

Table 1: The influence of LCC concrete properties varying with its components

Components of LCC	Properties influence
Refractory aggregate	Capacity of absorption, ostensible density, thermal conductivity, range of temperature of utilization
Super aluminum cement	Rheological properties – capacity of processing by casting, vibration, flowing, mechanical resistance
Dispersing agents	The thixotropy of the mixture
Reactive oxides (Al_2O_3, SiO_2, MgO, Cr_2O_3, TiO_2)	Flowing, volume stability, ostensible density, resistance to abrasion
Granulometric distribution Relation between grains >1 mm and fine fraction <1 mm	The work: - torcretation – adherence - casting – homogenous flow Homogenous structure

The production of concretes with low content of hydraulic binder is made by casting – vibration, either within the shapes, thus resulting in prefabs, or directly, at the very place used by the beneficiary, using encasements after that being treated until the maximum temperature, following a diagram, according to the quality of the concrete.

3. THE MAIN CHARACTERISTIC OF LCC AND ULCC REFRACTORY CONCRETES

The classical concretes are generally characterised by the content of Al_2O_3, which reflects both their refractarity and other physical properties. Regarding the concrete with low content of cement (LCC) and very low content of cement (ULCC) the content of Al_2O_3 is no longer enough for this characterization, other oxides (with smaller percentage of participation) having a great influence on the physico-chemical characteristics.

In table 2 the main oxides in LCC and ULCC concretes are presented, compared to a classical concrete, with the same content of Al_2O_3 and tabular alumina aggregate.

Table 2: The main oxides in LCC and ULCC concretes compared to a classical concrete, with the same content of Al_2O_3 and tabular alumina aggregate

The main oxides	Classical concretes	Concrete with low cement	Concrete with very low cement

The aggregate	**Tabular alumina**	**Tabular alumina**	**Tabular alumina**
Al_2O_3, %	90	90	88
CaO, %	5	1,1	0,3
SiO_2,%	2,8	4,0	7,5
Fe_2O_3, %	1,0	0,15	0,1

The high content of SiO_2 of LCC and ULCC concretes comes, in this case, from the ultrafine powders. In case of using other aggregates (chamotte, bauxite etc.) the content of SiO_2 can be higher to Al_2O_3 content's detriment.[2]

Through the dossage of ultrafine powders an optimum percentage of SiO_2 can be achieved, which is important because the bending resistance at temperature and the softening temperature of LCC and ULCC concretes depend of the percentage of anortit formed with calcium aluminates at 1350°C (fig. 5), and the one of ULCC depends on the content of mulit formed with Al_2O_3 at 1300°C (fig.6).

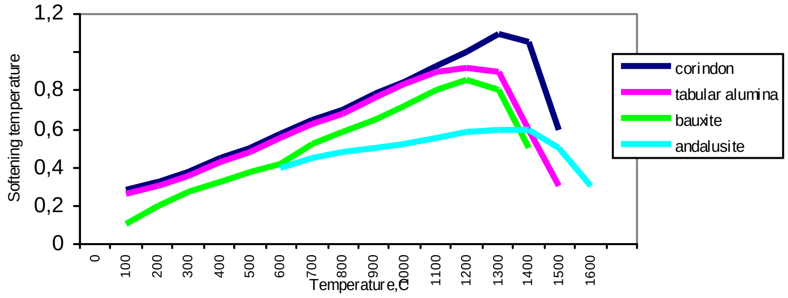

Figure 5: Softening temperature of burned LCC concrete, with various aggregates: 1 – corindon, 2 – 2 tabular alumina, 3 – bauxite, 4 – andalusite

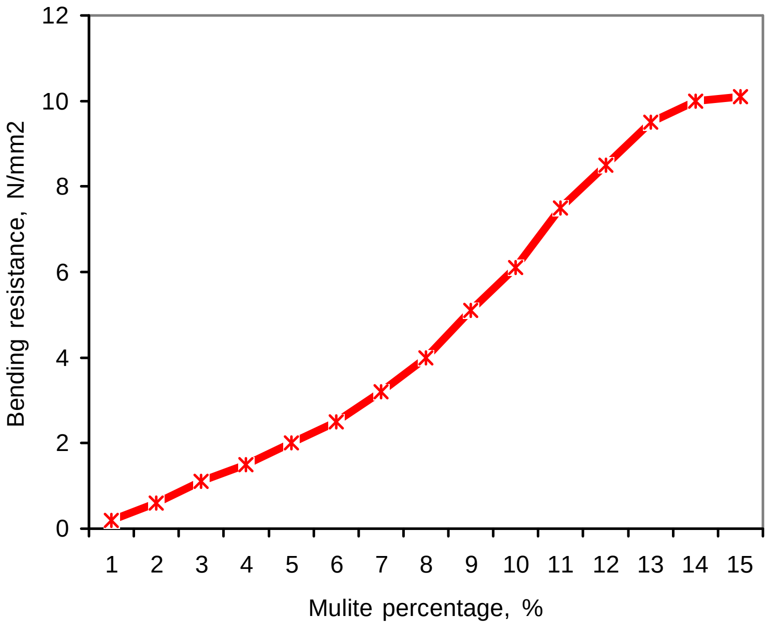

Figure 6: Influence of mulite percentage on the bending resistance at 1500°C of burned ULCC concretes

The ratios of CaO and Fe_2O_3 comming from cement, respectively the impurities of the aggregate, influence the bending resistance and corosion resistance of concretes. Due to the small percentage of CaO and Fe_2O_3, LCC and ULCC concretes have, compared to classical concretes, a higher resistance to chemical corosion, sometimes even better than burned shaped products.

All the classical concretes present, around the critical temperatures, (300 - 1200°C) a drop in mechanical resistance, wich can go up to 75% from the initial resistance, and which is provoked by dehydration of hydroaluminates of calcium, and successive transformations they endure until the beginning of sintering.

In case of LCC and ULCC concretes, instead of this dropping resistance there is a constant increasing, because, due to the presence of tripoliphosphate of aluminum the preponderance of gellic phase is insured, within the compact structure formed by the aggregate and the ultrafine powders, and wich, with the increasing temperature, crystallize forming gibbsit şi boehemit. Because of this, the dehydration of crystaline hydrates can not cause, in low temperatures area, up to 500 - 600°C , the policondensation of phosphates coming from the reaction of sodium tripoliphosphate compounds, which fights the drop of resistance due to phase transformations and mentains its values on an ascending curve, until CA şi CA_2 appear, when a new increase occurs.[3]

Although at the temperature of 1000°C all the compounds are completly dehydrated, and CA şi CA2 are formed, the increase of mechanical resistance is mentained through the double phosphates of calcium and potasium chrystalization and sodium salts until the beginning of sintering, when the increase of the resistance is high.

The variation of resistance to compression in low temperature after burning at various temperatures, of both classical concrete and LCC şi ULCC concretes with various aggregates, is shown in fig.7.

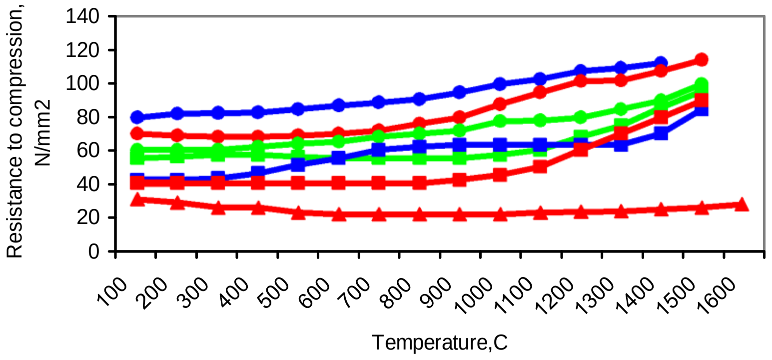

Figure 7: Resistance to cold compression, with various aggregates:

______ – corindon
______ – tabular alumina,
______ – andaluzit for the following concretes:
● ULCC concrete, ■ LCC concrete, ▲classic concrete

There can be seen that the values of resistance to compression of LCC concrete up to 1300°C are similar to the ones of burned shaped products and far better than in the case of classical concrete. The curves for ULCC concrete show that, regardless of the aggregate, its resistance to compression is much higher than LCC, or classical concretes, or burned shaped products.

Resistance to bending in heat is also increased compared to burned shaped products and classical concrete (fig. 8).

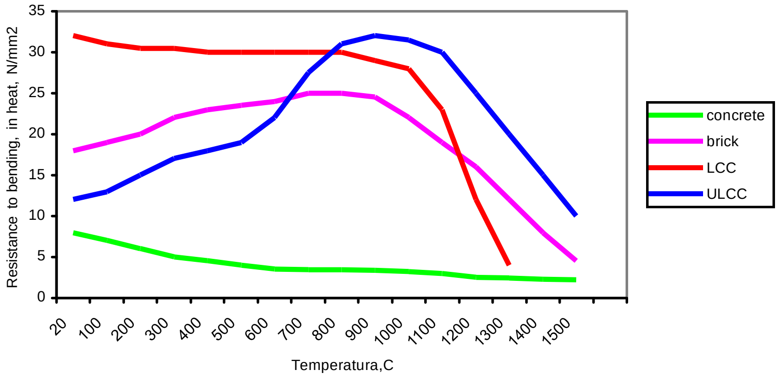

Figure 8: Resistance to bending in heat: 1 – concrete, 2 – brick, 3 – LCC concrete, 4 – ULCC concrete corrindonic aggregates

A great influence on heat resistance is dued to the mulit quantity formed in the proccess, as well as the drop of CaO percentage in the concrete (fig.9).

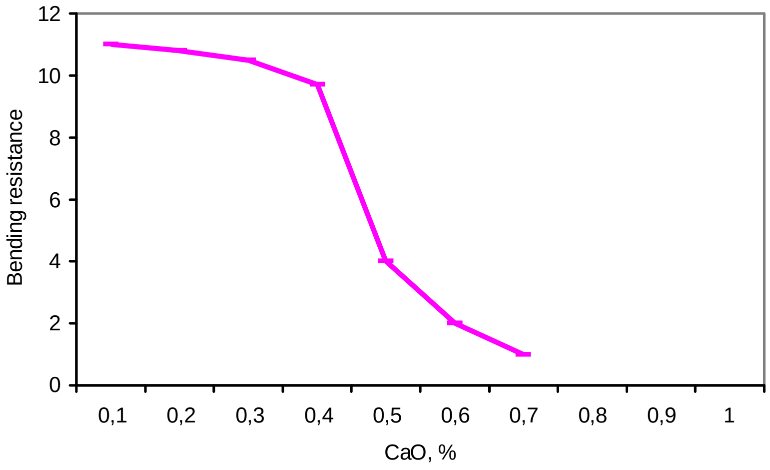

Figure 9: Influence of CaO ratio on the bending resistance at 1500 C, of a burned ULCC concrete

Due to the high values of mechanical resistance, internal tensions and pores distribution, LCC and ULCC concretes have a better impact resistance than classical concretes and burned shaped products, reaching over 50 heading-cooling cycles, when the aggregate is corrindonic or tabular alumina.

4. GRANULOMETRIC DISTRIBUTION

Producing dense refractory concretes, of high quality is determined so chemical purity of components, the their dosage as granulometric composition of mixture that aims to obtain a largest compactness.

By pursuing the granulation we reach to get as much compactness as possible. This generally characteristic depends both on the distribution, and the shape of the grains. Compounds of aggregates of splintery shape sometimes have a double surface compared to the spherical ones, thus needing more water to be prepared. To get a high resistance to bending, the rough surfaces of the grains are more advantageous than the smooth ones. The rate of fine aggregate from refractory concretes must be higher than that of ordinary concretes, because they are more profitable to the purpose and provide a relief of sintering process between the aggregate and the cement. The maximum dimension of the aggregate enclosed in refractory concretes is mainly determined by the section of the pieces to be made; it does not have to be bigger than 1/4 - 1/5 from the minimum dimension of the concrete piece. In common practice there are not used aggregates with a higher diameter than 40 mm. In the case of corundum aggregates the maximum dimension reaches just 10 mm.[4]

To obtain maximum capacity of concretes the granulation of the compound needs to approach the ideal curves established by Fuller - Bolomey. In fig. 10 we can see the ideal granulation, in volumes, for the aggregates used for refractory concrete. Establishing the granular distribution according to the maximum section of the concrete piece, the dosages between the aggregate and concrete will be of 3-4,5 volumes of aggregate for a volume of cement.

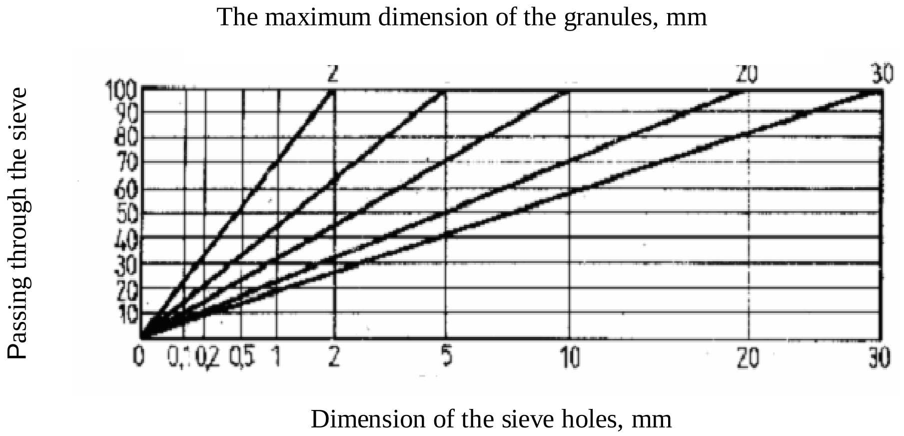

Figure 10: Ideal granulosity, in volumes, for refractory aggregates used in refractory concretes

The granulometric distribution of refractory distribution can also be established through the following formulae:

$$y = 100 \cdot \sqrt{d / D} \qquad \textit{Fuller's formula} \qquad (1)$$

$$y = A + (100 - A) \cdot \sqrt{d / D} \qquad \textit{Bolomey's formula} \qquad (2)$$

$$y = 100 \cdot (\frac{d}{D})^n \qquad \textit{Gummel's formula} \qquad (3)$$

where: d – dimension of particles

D – maximum dimension of particles

A – coefficient, according to the type of aggregate, A = 8 – 12

n – coefficient, n = 0.2-0.4 – 0.3-0.5. For Gummel n = 0.1 – 1

Figure 11 illustrates the areas of fluidity of the granule compounds in a ternary diagram. As we can see, the particles under 0,045 mm are called fine, the ones between 0,045 – 1 mm are intermediary, and the ones bigger than 1 mm are called granules.

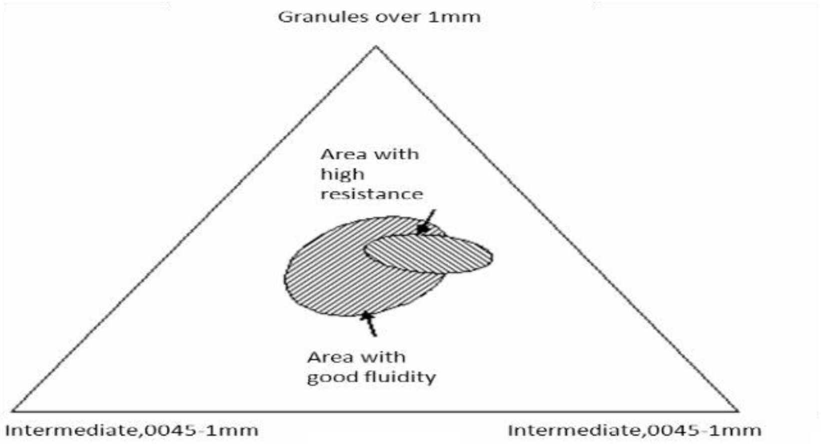

Figure 11: Areas of fluidity of granular compounds

The study of physical properties of refractory concretes obtained from the same raw material, but having different granulometries has shown some general rules:

- compositions with high percentage of fine have a big mechanical resistance, but a high contraction when burned;
- compositions with 55-70 granules and 30-45% fine (with no intermediary ratio) lead to good compacticitie and low contractions;
- compositions with 70-80% granules have a good resistance to mechanical impact;
- compositions with fine ratio, or with granules (provided that the different granular components have the same contraction when burned) lead to reduced permeability.

5. POROSITY

One of the most important properties of concretes is the ostendible porosity. This gives indications on the resistance to impact, corosion and infiltration. According to the place we use the concretes, the ostendible porosity needs to be controled, to provide the infiltration of melt metal, and, implicitly, the corosion.

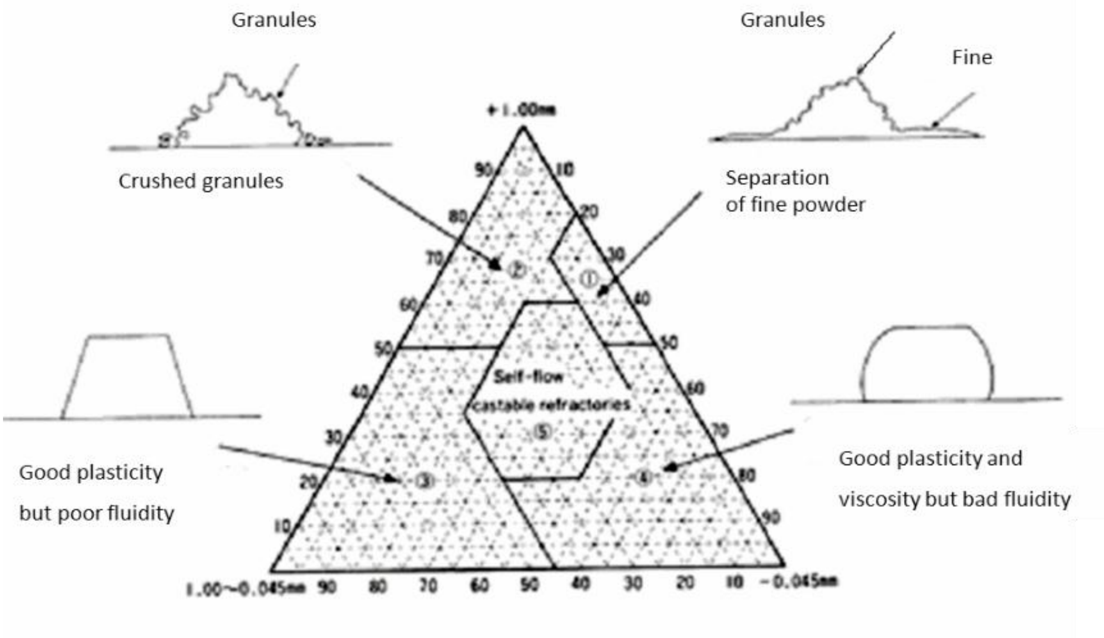

Figure 12: Influence of the dimenssion of particles on fluidity

The lower ostendible density of tabular alumina is dued to the small pores (closed) (<10µm), which do not allow the infiltration of slag, but improve considerably the resistance to impact of the aggregate.
Tabular alumina has a high chemical purity (Al_2O_3>99,4%), which improves the resistance to usage for concretes for trenches.

Classic refractory concretes, due to the high content of cement, have, when raw, an ostensible porosity around 9 – 10%. When the content of cement is higher, the ostendible porosity when raw, decreases. This porosity increases during heating, due to dehydration and phase transformations of calcium hydro-silicates, reaching a maximum of 30-35% and dropping then to 23-26% as ceramic conection and sintering occur.[4]

Both LCC and ULCC concretes, although the cement content is reduced, have reduced porosity, when raw around 6-9%. This is due to filling the intergranular spaces with very fine ratios of powders, the micropores still remained being filled with gelly phase. We have to mention that the ostendible density of LCC and ULCC concretes is high particularily because of that, reaching up to 3-3,2 g/cm^3 (according to the nature of the refractory aggregate and temperature). With the increase of temperature LCC and ULCC concretes have a small increase in porosity, compared to ordinary concretes, reaching to max. 14-18% (fig.13)

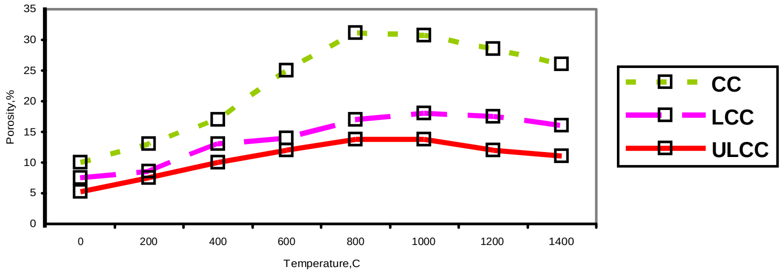

Figure 13: Porosity according to temperature for:

1 – classic concrete, 2 – LCC concrete, 3 – ULCC concrete with tabular alumina aggregate

This is dued to the small ratio of hydration water in LCC and ULCC concretes compared to classic concrete, and the preponderance of gellic phase which increases very little the porosity, with the increase of temperature, through the transformations that occur.Thus, LCC concrete has a porosity of 11-14%, which is a far better porosity compared to classical concretes - 25-27%.

The permeability of concretes depends mostly on the size of the pores and less on the total content of pores. In classic concretes, even if after heating the porosity is high until 800°C, the porosity is very low. Over this temperature the permeability increases, due to the increase in crystals, fact that leads to the decrease of internal specific intern surface, and to intern structural changes of dehydrated product of cement.[4]

For temperatures over 1000°C, the permeability of classic concrete reaches the values of other refractory materials. The same thing happens in case of LCC and ULCC concretes, but with smaller values in the area of low temperatures. Over 800°C, the permeability of concretes increases considerably, as at temperatures of 1200-1300°C its value can be compared to a classic concrete.

The low values of permeability to gass of LCC and ULCC concretes, until 800°C lead to the need to carefully choose the heating speed for the vaporization of water, unless special additives are used. Over 800°C the heating speed can be increased without the risk of explosion.

6. EXPANSION – CONTRACTION

During the heating of a classic concrete, especially at first burning, a series of contractions and expansions occur, initially provoked by dehydration and phase changes of the cement and the expansion – contraction of sinterized cement – aggregate system. Up to 1000°C the expansion of concrete is reversible, the concrete not having yet being made a ceramic conection.

Over 1000°C, and, especially from 1200°C up, due to ceramic conection and sintering of concrete, ireversible changes occur in the dimensions which firstly expand, and when the temperature reaches the refractarity limit of the concrete, or overcomes the temperature of aggregate burning, contract. The contractions occur mainly in chamotte aggregate concretes, when the heating temperature of the concrete reaches and overcomes the burning temperature of the chamotte. The well burned chamotte has, though, small contractions. Unlike the chamotte, the corundum or tabular alumina aggregates expand continuously almost to the limit of refractory, when contraction begins.

When cooling, the ireversible expansion or contraction reached at the maximum heating temperature, will contract over or under the initial dimensions, the values ranging betwen +1,5 and -0,6%. At a new heating, the concrete will reversibly expand to the maximum temperature of the first ireversible heating, which will be the value of maximum expansion for the next heating.

Within LCC and ULCC concretes the contraction determined by the low ratio of cement is compensated by the expansion of ultra-fine powders, making a neutral system for LCC, while for ULCC the trend is towards expansion. Thus, for LCC the variation of dimensions will be given by the expansion-contraction of the aggregate, which, when corrindonic or tabular alumina, begins expansion at 1200°C keeping linearly increasing, and when chamotte, will have a reversible expansion, followed, at 1200-1300°C by a contraction (which is partially compensated by the expansion of ultra-fine powders of SiO_2 at the transformation of α-quartz in tridimit around 873°C), reaching, at the maximum temperature of concrete usage (about 1350°C) aproximatively -0,3%.[4]

Usage of corundum or tabular alumina aggregates is not justified unless LCC concrete for high temperatures. In this case the concrete will have an almost continuous expansion, until a maximum of +0,8 - - 1% .

In ULCC concrete, the tendency to expand occurs regardless of the aggregate we use. When using the chamotte, at a temperature of usage for the ULCC concrete of 1600°C the mulit formed from 1300°C contracts, its contraction giving final expansions of up to +0,4%. For corindonic or tabular alumina aggregates values of expansion of +0,9 ... +1,26% at temperatures of 1600-1700°C occur.

In these conditions, the expansion gaps of LCC concrete clothings must be very carefully dimensioned, taking into consideration the fact that the values presented above are obtained in laboratory where the samples are heated on all their facets. In common practice we must take into consideration values of 70-90% from the theoretical value of expansion. Contraction gaps in the clothings are compulsory, regardless of the concrete or aggregate type.

For LCC concrete with chamotte aggregates these gaps are superficial for low volumes, but for higher values, we need to provide the expansion gaps with dimensions according to the medium reversibile expansion factor. This has values ranging from $40 \cdot 10^{-6}$/°C to $6 \cdot 10^{-6}$/°C. Even if the concrete contracts under initial dimensions, the contraction occured after the concrete had expanded.

Similarly, we calculate the expansion gaps for chamotte aggregate ULCC concrete.

7. REFRACTORINESS

Using superaluminum cements, the classic refractory concretes will have a variation of refractoriness due not only to the type of aggregate but also to its proportion within the compound. Both LCC and ULCC concretes, due to their low or very low content of cement and high proportion of aggregate and ultra-fine powders, have higher refractoriness than classic concretes with the same type of aggregate. We need to mention that LCC concrete is refractory just in case of replacing the ultra-fine powders of SiO_2 with Cr_2O_3 or Al_2O_3. From economic reasons we recommend the use of LCC concrete at temperatures of 1350°C, over this temperature ULCC concrete being the best solution.[5]

In table 3 there can be seen the values of refractoriness for different types of concretes.

Table 3: Values of refractoriness for different types of concretes

Characteristics	**Ttype of concrete**	**Aggregate,%Al_2O_3**				
		Chamotte 44-46	**Andaluzit 59-61**	**Chamotte 69-71**	**Corrindon 91-93**	**Tabular alumina 98-98,5**
Refractori-ness	Classic concrete	1460	1500	1670	1820	1850
	LCC concrete	1760	1790	1870	1930	2000
	ULCC concrete	1760	1800	1870	1950	2000
Maximum temperature of use	Classic concrete	1300	1400	1520	1750	1800
	LCC concrete	1550	1560	1600	1800	1900
	ULCC concrete	1600	1650	1650	1800	1900

8. CONCLUSIONS

In this paper we have reviewed the main features of LCC and ULCC refractories concretes: granulometric distribution, porosity, expansion-contraction, refractoriness.

Due to the high values of mechanical resistance, internal tensions and pores distribution, LCC and ULCC concretes have a better impact resistance than classical concretes and burned shaped products, reaching over 50 heading-cooling cycles, when the aggregate is corundum or tabular alumina.

Both LCC and ULCC concretes, although the cement content is reduced, have a reduced porosity, when raw around 6-9%. With the increase of temperature LCC and ULCC concretes have a small increase of porosity, compared to ordinary concretes, reaching to max. 14-18%

To get a high resistance to bending, the rough surfaces of the grains are more advantageous than the smooth ones. The rate of fine aggregate from refractory concretes must be higher than that of ordinary concretes, because they are more profitable to the purpose and provide a relief of sintering proccess between the aggregate and the cement.

The curves for ULCC concrete show that, regardless of the aggregate, its resistance to compression is much higher than LCC, or classical concretes, or burned shaped products.

Both LCC and ULCC concretes, due to their low or very low content of cement and high proportion of aggregate and ultra-fine powders, have higher refractoriness than classic concretes with the same type of aggregate.

From economic reasons we recommend the use of LCC concrete at temperatures of 1350°C, over this temperature ULCC concrete being the best solution.

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