

# IMPACT OF DISPERSANTS ON THE MECHANICAL STRENGTH DEVELOPMENT OF ALUMINA-SPINEL SELF-FLOWING REFRACTORY CASTABLES

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*The effect of four commercial dispersants on the properties of alumina-spinel self-flowing refractory castables was investigated. The self-flow value, water demand, physical and mechanical properties as well as microstructure of these castables were evaluated. The results showed that the polycarboxylate ether is the most effective dispersant in increasing self-flowability because of its electrosteric dispersion mechanism. By the use of proper amounts of polycarboxylate ether and sodium hexametaphosphate, the alumina-spinel self-flowing refractory castables with high strength and adequate working time were obtained. The microstructural evaluations showed that the  $CA_6$  was formed inside the grain boundaries of refractory castable after firing at 1500°C.*

## INTRODUCTION

Self-flowing refractory castable (SFC) is characterized by its consistency after mixing, which allows to flow and de-air without the application of external energy (i.e., vibration) [1]. Comparing with vibration refractory castable (VRC), SFC flows under its own weight. Therefore, it easily fills intricate forms and shapes without any external force. This makes the installation operation easier than VRC. Thus, fewer steps are required depending on the skill and awareness of the workers. Furthermore, small pore size, few mold defects, good service performance, noise-free action, saving man-power and time are among the advantages of SFC [1-5]. Consequently, the consumption of SFC has increased considerably [1, 2, 5]. Applications such as monolithic ladle lining, where the ability of pumping of the refractory material is critical for quick and easy installation has strongly influenced the use of SFC. Hence, alumina-spinel self-flowing castables have been used as steel ladle lining below the slag line because of increasing labor costs and the severe secondary steel-making environment in the ladle [6-11].

A few parameters have great effect on SFC development which, are the particle size as well as particle distribution, type of raw materials, and additives natures, such as deflocculating agents or dispersants. On the other hand, the additives interactions with the hydraulic agents during the hydration periods influence castable properties such as working time and initial mechanical strength. Therefore, it is necessary to optimize the type and quantity of additives used for any specific system [1, 5, 6. 12-15].

The main purpose of this work is to evaluate the influence of additives such as deflocculating agents on the self-flow characteristics of alumina-spinel self-flowing refractory castables. Additionally, the physical and mechanical properties of the refractory castables as well as their microstructure at high temperatures are investigated. For this purpose, four commercial dispersants such as; poly carboxylate ether (PCE), sodium polymethacrylate acid (PA) and sodium hexametaphosphate (HMP) were used and the results are presented.

## EXPERIMENTAL

## Raw materials and composition

The composition used for the preparation of alumina-spinel self-flowing castable is listed in Table 1. The chemical composition of raw materials used for this study is shown in Table 2. Also, three different dispersants were used in this study, their types and sources are listed in Table 3.

## Particle size distribution

The particle size distribution is calculated from the Andreasen's equation as Equation (1) [1]:

$$\text{CPFT} = 100 \times (d/D)^q \quad (1)$$

where CPFT,  $d$ ,  $D$ , and  $q$  indicate the cumulative percentage finer than, particle size, the largest particle size (5000  $\mu\text{m}$ ) and the distribution modulus, respectively.

Table 1. Raw materials and composition of alumina-spinel refractory castable studied.

Raw materials		Source (Type)	wt. %
Tabular Alumina	2-5 mm	Alcoa chemicals, (T-60)	60
	1-2 mm		
	0.5-1 mm		
	0-0.5 mm		
	$\leq 45 \mu\text{m}$		
Spinel	0.5-1 mm	White Circle, (Spinwhite 78)	23
	0-0.5 mm		
Reactive Alumina	$d_{50} = 1.90 \mu\text{m}$	Alcoa Chemicals, (CTC-20)	11
Calcium Aluminate Cement	$d_{50} = 3.03 \mu\text{m}$	Lafarge, (Secar-71)	6

Table 2. Chemical composition of used raw materials.

Oxide (wt.%)	Tabular Alumina	Spinel	Reactive Alumina	Cement
$\text{Al}_2\text{O}_3$	99.4	76-77	99.8	72.7
$\text{Na}_2\text{O}$	0.33	0.15	0.06	0.19
CaO	0.05	0.30	0.02	26.5
MgO	0.10	22-23	0.02	0.09
$\text{SiO}_2$	0.02	0.06	0.03	0.20
$\text{Fe}_2\text{O}_3$	0.10	0.10	0.03	0.11

Table 3. Type and source of dispersants used.

Additive	Type	Source
Polycarboxylate (PCE)	FS 10	S.K.W. Polymer
Sodium Polymethacrylate (PA)	Darvan 7S	Vanderbilt
Sodium Hexamethaphosphate (HMP)	-	Kimia Mavad

In order to achieve self-flow, the  $q$  values should be in the range 0.21 to 0.26. For the present study,  $q$  is chosen to be 0.24 [5]. Particle size distribution of the castable is represented in Figure 1.

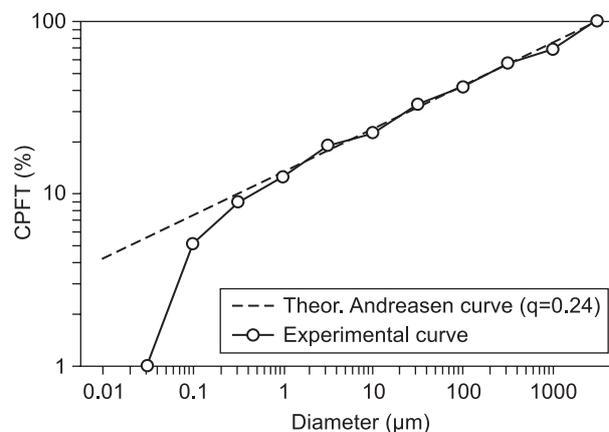


Figure 1. Theoretical and experimental particle size distribution of self-flowing refractory castable.

## Self-flow measurements

Self-flow tests were carried out, based on the ASTM C-1446-99 standard, to provide an index of castable flowability [16]. After dry mixing the batch for 30 s in a planetary mixer (Hobart), water (distilled) was added within 10 s while the mixer was running. The wet mixing was conducted for 5 min at a slow speed (Hobart, speed 1). Then, the castable was transferred to a sealed container and care was taken to keep the moisture constant. Ten minutes after water addition, the mixed castable was poured into a standard cone with a base diameter of 100 mm (ASTM C-230). The cone was then elevated to allow the mix to flow. After 60 s, the patty diameter was measured. The percentage increase in spreading diameter after 60 s was taken as the self-flow value (SFV) according to the following formula [16]:

$$\text{SFV} (\%) = (D_2 - D_1) \times 100 / D_1 \quad (2)$$

where  $D_2$  is the final average diameter after removal of mold and  $D_1$  is the initial diameter (100 mm). The castable is considered self-flowable when the above value lies within the range of 80 to 110% of the base diameter. In addition, working time was measured as the point at which the castable showed no movement under its own weight (SFV < 80%). During the SFV evaluation, the ambient temperature was controlled to be in the range of 20 °C to 24 °C [16].

## Castable preparation

The dry constituents of the castable were mixed for 4 min, water was added, and the whole composition was wet mixed for an additional 4 min. The mixture was cast into standard mold without vibration. After curing at

20°C and 90 % relative humidity for 24 h, the specimens were taken out of the mold, dried for 24 hrs at 110°C and fired at 1000, 1300 and 1500°C for 3 hours. Bulk density (B.D), apparent porosity (A.P), cold crushing strength (C.C.S), modulus of rupture (M.O.R) of the specimens were measured after drying and firing at each individual temperature. Bulk density and apparent porosity of dried and fired samples were determined by the water immersion method (in accordance with ASTM C 830-93). Also, modulus of rupture (3-point bend test) and cold crushing strength were performed in accordance with ASTM C 133-97. Bulk density, porosity and mechanical strength data presented in this article correspond to an average of five specimens for each composition and at each firing temperature.

#### Microstructural evaluations

In order to evaluate the microstructure, scanning electron microscopy (SEM) (Cambridge S-360) was performed on polished sections after gold coating. Energy dispersive X-ray spectroscopy (EDX) accompanied SEM observation to allow the identification of the crystalline phases.

## RESULTS AND DISCUSSION

Figure 2 shows the variation of SFV of the castable with increasing dispersants contents. In all cases, the amount of water was kept constant at 5.5 wt.%. It is clearly seen that dispersants type and addition level significantly impacts the castable SFV.

From Figure 2, one can see that the best flow values are obtained with PCE. Moreover, the optimum dispersant for maximum SFV is seen to be 0.1 wt.% for PCE.

Generally, the fluidity of a water-cement system is a function of attractive and repulsive forces between cement particles and fines' particles of the system.

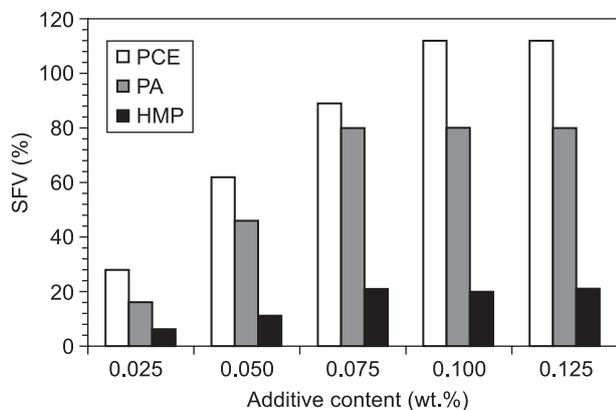


Figure 2. The effect of various dispersants on the refractory castable SFV vs. dispersant content (5.5 wt.% water was added to the castable).

Attraction leads to flocculation and low fluidity of the system. Repulsive between the particles gives dispersion and high fluidity. Dispersants or deflocculating agents are absorbed on the surface of the cement and other particles, increasing the zeta potential and promoting good dispersion due to the repulsion between positively charged grains. On the other hand, particles dispersion inhibits the formation of agglomerates that can hinder optimum particle packing and affect the final mechanical strength of refractory castable. Therefore, a high-strength dense refractory castables is obtained, with well dispersed fine-particles portions including alumina cement. The dispersion mechanism of polyacrylate (PA) is via electrostatic stabilization. The methacrylate molecules of this additive are distributed through a linear molecule ( $\approx 8-9$  nm). This structure lowers the dispersion efficiency when high-solid concentrations are involved by inducing bridging and depletion of flocculation among the particles.

As indicated by the manufacturer, comb structure of PCE results in a small molecule ( $\approx 3.0$  nm  $\times$  3.2 nm) composed of a highly charged main chain and a set of lateral uncharged chains that display a steric lubricating barrier. Therefore, PCE combines the advantages of high molecular weight polyelectrolyte (steric barrier and high charge density) with the superior mobility of short chain additives. Due to these strong electrosteric repulsive forces, the agglomerates of the particles are thoroughly broken up and the enclosed water in the agglomerates is released. The friction between particles is neutralized. Thus, the flowability of the refractory castable is increased, making the compound flowable with extremely low mixing water. So, the refractory castable changes to the SFC [13-15].

The SFV of castable with respect to the amount of water demand in the presence of the optimum amounts of two different dispersants was also investigated. Results are shown in Figure 3. Based on these results, PCE is more efficient deflocculating agent than PA in reducing the water demand of alumina-spinel self-flowing casta-

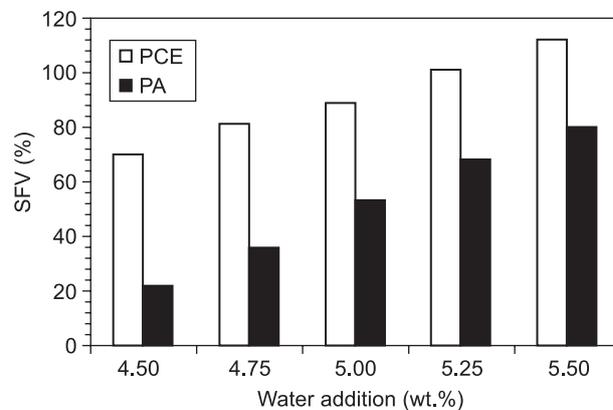


Figure 3. SFV of the refractory castable vs. total water consumption for optimum content PCE (0.1 wt. %) and PA (0.075 wt. %).

bles. The refractory castable with optimized amount of PA (0.075 wt.%) acquires self-flowing properties by the addition of 5.5 weight percent of water. Whereas, the same castable with optimized amount of PCE (0.1 wt.%) shows self-flowing properties by the addition of 4.75 weight percent of water. As a result, the reduced content of water by using PCE leads to higher densities, decreased porosity and higher strength compared to the PA based composition.

Figure 4 shows the effect of HMP addition (0.02 wt.%) on the C.C.S of the castable containing PCE optimum content after firing at different temperatures. It is clear that the HMP has a great effect on the strength development of the castables, so that the use of HMP in combination with PCE is able to improve the strength of the castable.

A very important characteristic is the green strength development of a castable. It is created by the formation of hydrates of the clinker phases. It is well known that the formation of the hydrate phases can be influenced by additives [2, 14]. On the other hand, the C.C.S of castable after drying is a useful indicator of hardening time [1, 2, 14]. Therefore, the hardening time of alumina-spinel refractory castable is changed by the use of HMP additive. Figure 5 shows the effect of HMP addition (0.02 wt.%) on the SFV-time curve of the refractory castable containing optimum PCE value. The obtained results show that HMP addition can affect these curves so that, addition of HMP decreases the working time of refractory castable composition.

The primary role of dispersants in deflocculated refractory castable system is to provide sufficient flow for placing at low water additions, necessary to conserve a compact structure. However, their impact influences the hydration of calcium aluminate cement, often retarding the precipitation reactions. This is particularly true in the case of highly efficient dispersing additives, necessary for high flow or prolonged workability, which utilizes electrosteric dispersion. PCE at level of 0.1 wt.%

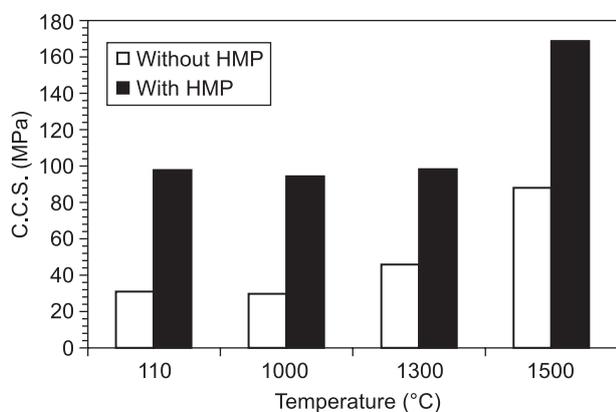


Figure 4. The effect of HMP (0.02 wt.%) on the C.C.S. of the refractory castable at different temperature (optimum content of PCE and 4.75 wt.% water was added to the refractory castable).

addition generally produces very high flow and high workability over time. Therefore, PCE proved to be the most effective retarding agent. The polycarboxylate ether molecules are absorbed on the fine particles; such as cement particles. Therefore, the reaction of cement and other particles that can hinder setting of castable is inhibited. On the other hand, it is found that higher contents of this additive have a disadvantage on the strength development. This phenomenon is related to the absorption of polycarboxylate ether molecules on cement particles. As a result, the bonding action of cement particles decreases. In order to shift the set time to an earlier stage and get good strength after drying, it is required to add an accelerator which again leads to a decrease in working time [1 and 2]. Therefore, HMP additive acts as an accelerator and decreases working time.

Generally, the first sequence in the setting of a castable is loss of flow, i.e. it becomes impossible to place. Hence, control of the flow and setting time has always been one of the most wanted but also perhaps the most difficult aspect of refractory castable technology. In practice, 30 up to 100 min can provide long enough working time for appropriate placement of castables [1, 4, 5, 7]. Although, the working time of these castables is decreased, it is sufficient for installation conditions and successful placement. Therefore, by the use of PCE (0.1 wt.%) and HMP (0.02 wt.%), the self-flowing alumina-spinel refractory castable with high mechanical strength and adequate working time can be obtained. The microstructure of the alumina-spinel refractory castable containing optimum content of PCE and HMP after drying is presented in Figure 6.

This figure shows high packing and well dispersed particles in microstructure, in which the fine particles such as reactive alumina occupy the voids between the coarse particles. This enables the decrease of porosity and an increase of the green strength. At low temperatures (110°C), the phases present in the alumina-

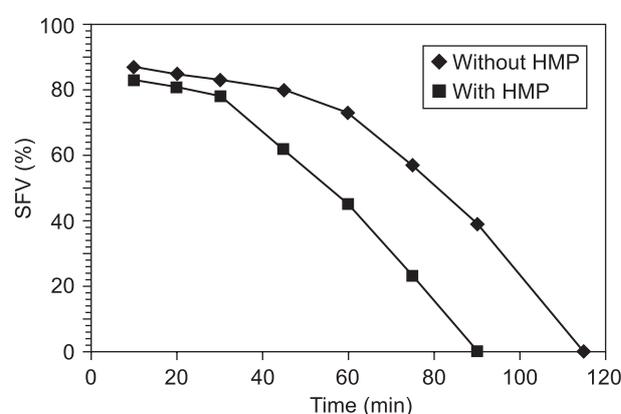


Figure 5. HMP addition (0.02 wt.%) on the SFV of the refractory castable containing PCE optimum as a function of time (4.75 wt.% water was added to the castable).

spinel refractory castable are: alumina tabular and spinel aggregate that linked together by castable matrix. Generally, matrix of these castable comprising of calcium aluminate cement hydrates together with reactive alumina and fine grains of spinel. The microstructure of the alumina-spinel refractory castable containing optimum content of PCE and HMP after firing at 1500°C is shown in Figures 7 and 8.

As shown in Figures 7 and 8, the microstructure of alumina-spinel refractory castable after firing at 1500°C comprises of alumina and spinel aggregates with some cluster of platy crystals on the surface of tabular alumina and spinel grains as matrix. The microstructure of these platy crystals is shown in Figure 9 and SEM/EDX analysis of these crystals is depicted in Figure 10. This analysis indicates that these platy shape crystals are in hibonite phase. Generally, the extra alumina reacts with calcium-aluminates from cement to form  $\text{CaO} \cdot 6\text{Al}_2\text{O}_3$  ( $\text{CA}_6$ ) crystals above 1450°C which is limited to the fines in the refractory castable matrix [17-19].

This calcium hexa aluminate provides an excellent bond linkage between grains in the matrix by an inter-

locking morphology, which upgrades the properties at 1500°C. By comparing the SEM photomicrograph with strength properties, it can be observed that formation of hibonite contributed to the development of castable C.C.S after firing at 1500°C. As a result of hibonite phase formation, other properties of refractory castable such as HOT M.O.R and creep resistance can be improved.

Hibonite phase have characteristics such as high stability in reducing atmospheres (e.g. CO), high chemical resistance in alkaline environment, and low wet ability by molten metals and slag (Ferrous and non-ferrous) [20 and 21]. Therefore, the castables containing this phase can be used at different industrial furnaces e.g. in the aluminum melting furnace (low wet ability by molten aluminum), the cement kiln (high chemical resistance in alkaline environment), the steel furnaces (high refractoriness and low solubility in iron containing slag) and in the petrochemical industry (stability in reducing atmospheres). The pre-cast shapes of these castables have also been developed for industrial application. Figure 10 shows pre-cast shape of alumina-spinel self-flowing castable as burner pipe for cement kiln. In spite

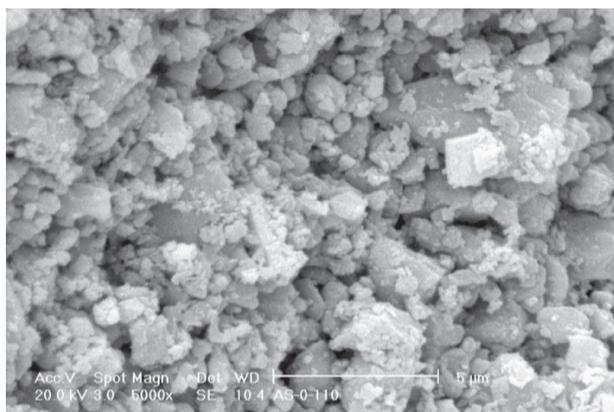


Figure 6. SEM photomicrograph of alumina-spinel refractory castable containing optimum additives (PCE and HMP) after drying.

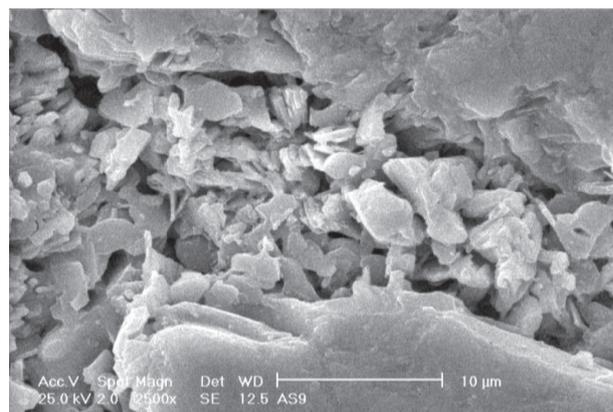


Figure 8. SEM photomicrograph of alumina-spinel refractory castable containing optimum additives (PCE and HMP) after firing at 1500°C.

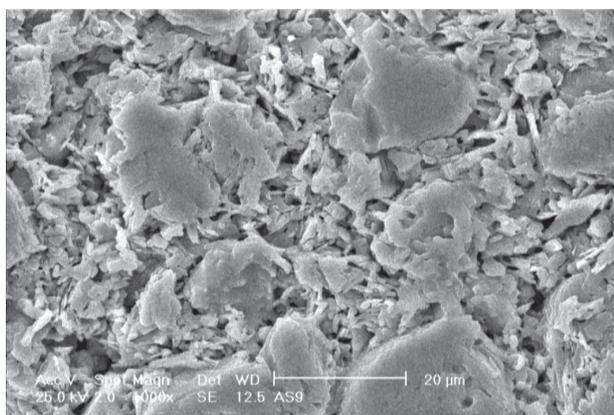


Figure 7. SEM photomicrograph of alumina-spinel refractory castable containing optimum additives (PCE and HMP) after firing at 1500°C.

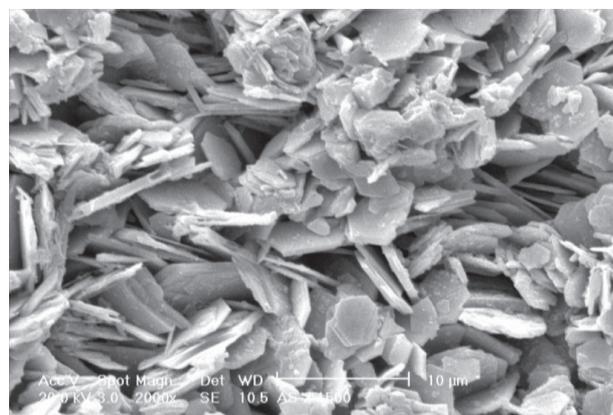


Figure 9. Platy crystals in the alumina-spinel refractory castable matrix after firing at 1500°C.

of the installation without vibration, the body structure of the mold was satisfactory. Also, the little pores were found in comparison with the V.R.C.

## CONCLUSION

In this work, self-flowing alumina-spinel refractory castables with low water consumption (4.75 wt.%) and high mechanical strengths are obtained. Strong influence that additives exert on the properties of these castables is confirmed. Among the dispersants investigated, polycarboxylate ether is the most effective in increasing self flowability in this system; its optimum addition amount is 0.1 wt.%. The electrosteric mechanism of polycarboxylate ether appears to promote higher flow ability in this system. The results also indicate that the sodium hexametaphosphate has a great effect on the green strength of the castable. As a result of polycarboxylate ether addition in combination with sodium hexametaphosphate, the mechanical strength of alumina-spinel refractory castable is increased. In

samples fired at 1500°C, platy crystals of  $CA_6$  were detected inside the grain boundaries of tabular alumina and spinel grains. This phase is able to improve the properties of these refractory castables.

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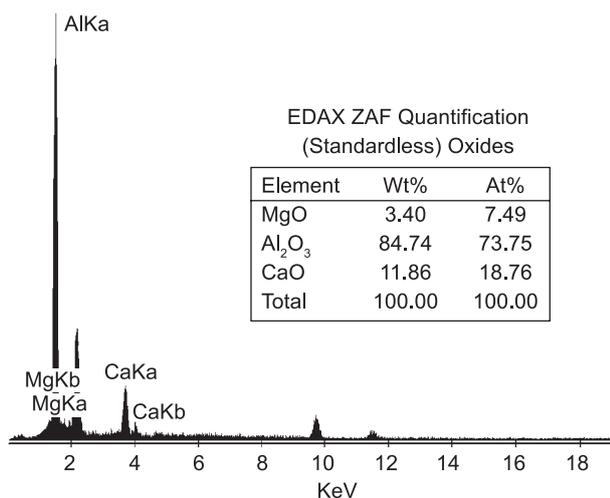


Figure 10. SEM/EDX analysis of platy crystals in Figure 8.



Figure 11. Pre-cast shape of alumina-spinel self-flowing refractory castable for using as burner pipe in cement kiln.