

Effect of silica sol of different routes on the properties of low cement castables

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Abstract. Silica sols synthesized through different routes viz. inorganic, organic and ion-exchange routes, have been incorporated in the low cement alumina castable composition in various proportions and cast samples in the form of 2 inch cube briquettes were prepared. The cast briquettes after curing were subjected to heat treatment at various temperatures. The effect of different sources of such sols on the important physico-mechanical properties of the castables such as bulk density, apparent porosity, compressive strength, volume shrinkage and residual strength after spalling have been studied. Some of the selected samples were also subjected to microstructural evaluation. It is observed that silica sol synthesized through cation exchange routes has significant beneficial role on the properties of castable with 3% addition.

Keywords. Low cement Al₂O₃ castable; silica sol; ion exchange.

1. Introduction

Originally, all conventional refractory castables were bonded with calcium aluminate cement containing CaO content up to around 20%. Low melting liquid phase formation in the system, Al₂O₃-SiO₂-CaO, including gehlenite and anorthite at working conditions significantly affects the high temperature properties of such high cement bonded conventional aluminous castable (Studart *et al* 1999). In addition to the above disadvantageous properties of high cement bonded conventional castable, it requires a high water demand on mixing, resulting low density and high porosity products (Kendall 1995). These drawbacks led to the development of low cement castable (LCC) containing 1.5–2.5% CaO. The principles behind this development of LCC and their improvement in regard to physical and thermomechanical properties have been widely reported (Clavaud *et al* 1983, 1984, 1985; Eguchi *et al* 1989; Masanyk *et al* 1993). In the beginning, calcium aluminate cement was partly replaced with ultrafine oxide powders such as SiO₂, Al₂O₃, TiO₂, Cr₂O₃ to produce coagulation bonding from the close contact of colloid particles by means of Vander Waal's force (Li and Ye 1992). According to DLVO theory (Studart *et al* 1999), a repulsive force occurs when the particles approach each other due to overlap of electrostatic double layers. Gauckler *et al* (1999) and Studart *et al* (2002) recently reported that coagulation mechanism involve the modification of the

nature of forces acting among fine particles from typically repulsive to attractive forces. Dispersion technology using superfine oxide powder improve the quality of low cement castable including its flow properties. In a powder water dispersion system, electrostatic double layers form on the solid-liquid boundary. Their interaction force varies depending on the concentration of those ions determining the surface potential such as H⁺ and OH⁻ for metal oxides. Thus, the flow properties vary with pH in the aqueous solution. Amongst many kinds of superfine oxide powder, superfine powder of alumina and silica have been the basic materials in developing low cement castable (LCC). Superfine Al₂O₃ used in LCC must have particle diameter 4–5 μm and specific surface area of around 1 m²/g. Fumed silica of high purity is the most preferred available super fine silica successfully used in LCC compositions for many years. Superfine powder incorporated LCC formulations are available in many literatures (Myhre 1994; Kang *et al* 1995; Jones 1998) where effect of change in dispersion system, granulometry and particle morphology on flow behaviour are discussed. Recently different kinds of sols which form coagulation bonding have been tried as binder in low, ultralow and no cement bonded refractory castable compositions. Amongst them use of water based colloid (colloidal silica) in alumina containing castable is becoming most popular due to its superior thermo mechanical properties (Roy and Banerjee 1997; Banerjee 1998; Das *et al* 2002).

Many methods are known for synthesizing silica sol (Ailer 1959; Freidenberg and Khvorov 1989). In the present investigation, silica sols are synthesized by different

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routes and incorporated in different proportions to a low cement castable composition made from white fused alumina aggregate, microfine Al_2O_3 and high alumina cement. Effect of such silica sol addition on the important properties of low cement castable have been studied and discussed in this paper.

2. Experimental

2.1 Synthesis of silica sol

Silica sol of inorganic route (system A) was prepared by thorough mixing of 10% NH_4Cl and 10% Na_2SiO_3 solutions. After removal of electrolyte, the sol was dispersed in aqueous medium by centrifugal action. System 'B' (silica sol of organic route) was prepared by mixing 1 : 1 volume of tetraethoxy silane and ethanol followed by slow addition of 1 : 1 NH_4OH solution with constant stirring. The sol was dried and then dispersed in alcohol medium. Silica sol of ion-exchange route (system C) was prepared by passing 10% Na_2SiO_3 solution through H-form of cation exchange column. The sol thus obtained was slowly evaporated to increase the solid content. pH of each sol was maintained at 8 by control addition of 1 : 1 NH_4OH solution. It was observed during preparation of silica sol that below pH 8, complete formation of silica sol did not occur and it had gone into the solution. Above pH 8, there was agglomeration of sol particles and gelatinous precipitation occurred which ultimately reduced the yield. In view of above, pH of each sol was maintained at 8.

2.2 Sample preparation and testing

Major refractory raw materials such as white fused alumina (supplied by Carborundum Universal Ltd), high

alumina cement (supplied by ACC Refractories), and microfine alumina (supplied by Indian Aluminium Co Ltd) were tested and intimately mixed following the batch formulation given in table 1.

Test samples of 2.5 cm cube were prepared by vibro-casting technique following IS 10570 (1983). The samples were kept in saturated humidity for 24 h followed by water curing for another 24 h and then heat treated at different temperatures for 2 h. Compressive strength of all the samples were measured using universal testing machine as per IS 1528: part 4 (1997). Bulk density, apparent porosity and linear changes were determined following standard methods. Spalling test was conducted by keeping the heat treated samples at 1000°C for 10 min followed by placing it in open air for next 10 min as per IS 1528: part 3 (1997). After 5 complete cycles, compressive strength of the samples were measured. Scanning electron microscopy was utilized using IEO electron microscope of model S440 to study the microstructure.

3. Results and discussion

The chemical analysis of the raw materials used in this investigation is provided in table 2. Gravimetric method was utilized to determine SiO_2 and Al_2O_3 whereas Fe_2O_3 , CaO and MgO were determined volumetrically (Hillebrand and Lundell 1953).

It may be seen from table 2 that white fused Al_2O_3 which is produced from fusion of calcined alumina has a very high purity (99.38 wt% Al_2O_3). Microfine Al_2O_3 used in the castable formulation is also of purer variety (99.58 wt% Al_2O_3) with 6–8 μm average particle diameter and α - Al_2O_3 content more than 95%. High alumina cement was analysed by X-ray diffraction and found to consist of CA and CA_2 as major, C_{12}A_7 ($\text{C} = \text{CaO}$, $\text{A} = \text{Al}_2\text{O}_3$) and α -alumina as minor phases (Das *et al* 1997). The specific surface area measured by the air permeability method was around $3150 \text{ cm}^2/\text{g}$.

Table 1. Batch formulation.

Sample code		Raw materials (wt%)					
		White fused alumina			High alumina cement	Microfine Al_2O_3	Silica sol
		C	M	F			
Without sol	I	50	20	13	7	10	–
System A (Sol of inorganic route)	IA	50	20	13	7	9	1
	IIA	50	20	13	7	7	3
	IIIA	50	20	13	7	5	5
System B (Sol of organic route)	IB	50	20	13	7	9	1
	IIB	50	20	13	7	7	3
	IIIB	50	20	13	7	5	5
System C (Sol of ion exchange route)	IC	50	20	13	7	9	1
	IIC	50	20	13	7	7	3
	IIIC	50	20	13	7	5	5

C = coarse, M = medium, F = fine.

Table 3 shows that compressive strength values are increased by adding silica sol and the values are maximum in case of systems A and C. The ultrafine particles are dispersed between the refractory grains and formed a coagulated hydraulic bond in presence of silica sol which might have improved the strength. No significant reduction in compressive strength value at intermediate temperature of heating was observed. The reaction product of silica sol with hydrated calcium aluminates during hydration of LCC arrests strength retrogression both at ambient and intermediate temperatures during heating of castable. This phenomenon was also observed by Midgley (1980) who found this reaction product as stratlingite ($\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2\cdot\text{H}_2\text{O}$).

For comparison, the compressive strength results of 1500°C heated samples are graphically represented in figure 1. It may be observed from this figure that the compositions with silica sol of ion exchange route (system C) gives better strength than systems A and B. Strength of system B is inferior to both A and C. It may also be seen that 3% silica sol in all the three cases gives the optimum results. Probably, it is due to the simultaneous effect of coagulation bonding contributed by silica sol and hydraulic bonding contributed by calcium aluminate cement hydrated in presence of water coming from silica sol. In case of less sol (1%), coagulation bonding is incomplete and in case of more sol (5%) and reduced microfine alumina content, the matrix becomes very porous with inadequate compactness. Hence combination of 3% silica sol and 7% microfine Al_2O_3 may be con-

sidered as optimum additive content for getting all desirable properties. The compressive strength was found to be maximum at 1500°C for all the compositions. This may be due to the reason that when fine particles of amorphous silica generated during heating reacts with microfine alumina present in the castables, a network of mullite needles develops at higher temperatures which strengthen the matrix. The similar observation was also made by Pivinskii (1995). The results of variation in bulk density, apparent porosity and linear changes in the temperature range 1200–1500°C are given in table 4.

It may be observed that BD increases with heating due to gradual formation of ceramic bond and the value is maximum at 1500°C for all the compositions. Due to increase in BD, the AP value expectedly decreases. The percent linear changes was found to be within tolerance limits. The value is below 0.5% at 1200°C and below 1.5% at higher temperatures. Further the results of table 4 have shown that addition of 3% silica sol of ion exchange route (system C) favourably influenced all these properties.

Table 5 indicates the residual strength after spalling test of heat treated samples. It is found that strength retention is much better in case of system C.

Scanning electron micrographs of selected samples are shown in figures 2a–d. It is found that better compactness

Table 2. Chemical analysis of the raw materials.

Chemical constituents (wt%)	Raw materials		
	White fused Al_2O_3	High Al_2O_3 cement	Microfine Al_2O_3
Al_2O_3	99.38	73.30	99.58
SiO_2	0.13	0.95	–
Fe_2O_3	0.12	0.20	–
CaO	–	24.50	–
MgO	–	0.45	–
Loss on ignition	0.34	0.35	0.32

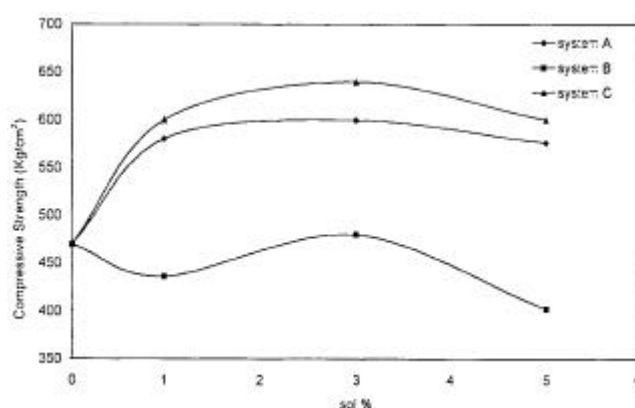


Figure 1. Compressive strength of 1500°C heated samples vs sol% of various routes.

Table 3. Compressive strength in relation to heating temperature.

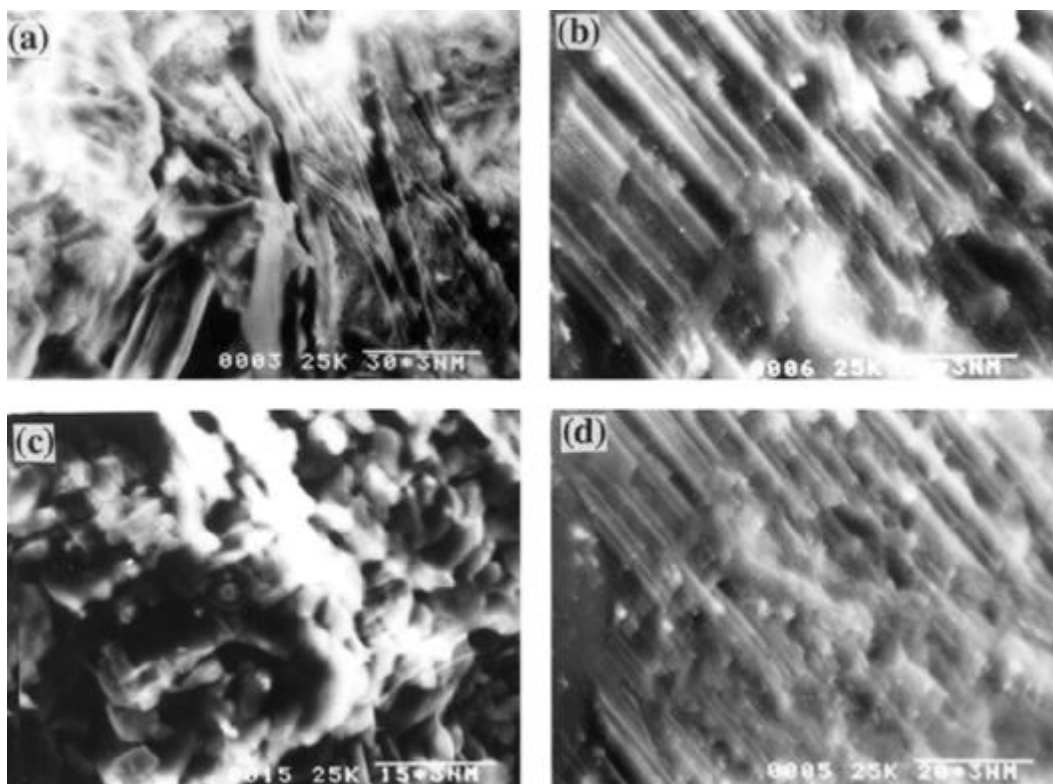
Temperature (°C)	Compressive strength (kg/cm ²)									
	Sample code									
	I	IA	IIA	IIIA	IB	IIB	IIIB	IC	IIC	IIIC
110	339	400	430	415	260	276	226	330	380	320
800	245	410	426	405	305	321	310	418	426	402
1200	207	395	402	380	286	298	290	390	398	386
1400	245	430	456	402	370	396	310	486	502	480
1500	470	580	600	576	436	480	402	600	640	600

Table 4. Bulk density (BD), apparent porosity (AP) and linear changes (LC) of castables in relation to heating temperatures.

Heating temperature (°C)	Properties	Sample code									
		I	IA	IIA	IIIA	IB	IIB	IIIB	IC	IIC	IIIC
1200	BD (g/cm ³)	2.65	2.55	2.61	2.58	2.55	2.58	2.55	2.65	2.70	2.65
	AP (%)	25.9	24.2	23.9	24.5	25.3	25.0	25.8	23.2	22.8	23.0
	LC% (-ve)	0.28	0.26	0.28	0.26	0.30	0.32	0.35	0.26	0.28	0.29
1400	BD (g/cm ³)	2.75	2.78	2.80	2.70	2.65	2.70	2.68	2.78	2.84	2.82
	AP (%)	23.5	22.6	21.8	22.0	22.80	22.0	22.5	19.0	18.5	18.8
	LC% (-ve)	1.05	1.21	1.25	1.28	1.26	1.22	1.25	1.21	0.98	1.25
1500	BD (g/cm ³)	2.82	2.85	2.90	2.80	2.70	2.78	2.72	2.90	2.92	2.88
	AP (%)	22.6	18.8	18.6	19.0	19.1	19.0	19.5	12.5	12.0	12.8
	LC% (-ve)	1.20	1.28	1.26	1.22	1.30	1.35	1.38	1.28	1.26	1.29

Table 5. Residual strength (%) after spalling test in relation to heating temperature.

Temperature (°C)	Residual strength (%)									
	I	IA	IIA	IIIA	IB	IIB	IIIB	IC	IIC	IIIC
1200	81.8	83.6	84.6	80.8	78.0	78.8	78.2	86.6	88.0	86.8
1400	70.5	78.8	79.0	78.5	70.2	70.8	70.2	84.4	86.0	84.8
1500	78.0	80.5	82.0	83.1	75.0	76.8	75.2	86.8	88.5	87.8

**Figure 2.** SEM photographs of samples heat treated at 1500°C: (a) sample without silica sol, (b) sample with silica sol of system A (inorganic route), (c) sample with silica sol of system B (organic route) and (d) sample with silica sol of system C (ion-exchange route).

of matrix with uniform distribution of mullite crystals occur in case of system C. It may be said that cation exchange route generates silica sol of smaller particle size which helps ceramic bond formation through mullitization in a more uniform way.

4. Conclusions

From the present investigation, the following conclusions are drawn:

- (I) Silica sols of inorganic and ion exchange routes improve the desirable properties of castable significantly in comparison to silica sol of organic route.
- (II) In both systems A and C silica sol is found to be more beneficial when the content is 3%.
- (III) Considering all the properties and microstructure of castables, silica sol of cation exchange route may be considered more effective.

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