

THE PROPERTIES OF A LOW CEMENT CASTABLE CONTAINING CHEMICALLY PREPARED HYDROUS SPINEL

SUNANDA MUKHOPADHYAY, TARAK NATH SEN, SK. MOMBASSAR HASSAN, PANCHUGOPAL PAL

College of Ceramic Technology, 73 A.C.Banerjee Lane, Kolkata - 700010, India

E-mail: msunanda_cct@yahoo.co.in

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Magnesium aluminate gel precursor has been synthesized by rapid co precipitation technique at a relatively low temperature. This gel exhibits the evolution of spinel phase at significantly lower temperature than solid state sintering; however it is associated with secondary phase like corundum and periclase at higher temperature. The gel has been incorporated in different concentration 0.5-4.0 wt.% to a high alumina based castable to fabricate in situ spinel-alumina monolithic refractory. Uncontrolled agglomeration and an enormous amount of -OH, -NH₂ and C=O groups associated with the precursor gel indicates a serious apprehension about the performance of the castable. Nevertheless an optimum amount of 2.0 wt.% of spinel gel renders a satisfactory role towards the physical properties of the castable. The microsilica content of the original batch should be reduced to eliminate the detrimental CaO-Al₂O₃-SiO₂ phase generated in the matrix.

INTRODUCTION

Keeping pace with the continuous technological developments taking place in iron and steel industries, the refractory industry is also stepping forward through a great deal of metamorphosis [1]. During the last couple of year a noticeable advancement has been achieved in the fabrication and application of monolithic refractories, specially castable like low, ultra low and no cement types [2,3]. While the chemistry of such materials governs the reaction and bonding of the matrix, the particle size distribution decides how far it would behave as a self flow material with requisite high temperature properties[4]. Thus it has been possible to optimize the cement content of castable and control its rheology by incorporating a perfect package of micron and sub micron size particles with selective additives and deflocculants [5-8]. Some researchers proposed another category of castable bonded by chemically prepared gels. These monoliths assist the self flow criteria, improve the spalling resistance and betoken the possibility of cost and energy saving [9-11].

Refractory spinel bonded castables are nowadays used widely in the steel ladle linings [12,13] to replace high alumina bricks. Both preformed and in situ types of this castable are popularly used in the commercial practice [14-17] even in concast tundishes, lance pipes, degasser snorkels and electric arc furnaces where slag corrosion and erosion resistances are of prime concern. We have already reported the newer variety of in situ

spinel-alumina castables prepared by hydrated magnesium aluminate gels [18-24]. Instead of magnesia fines (used traditionally), those castables are bonded with sol gel derived and conventionally coprecipitated spinel gels [25,26]. A modified method for preparing magnesia aluminate gel had been suggested by some authors [27,28] long back by a rapid coprecipitation technique at remarkably low temperature than the traditional rout [26].

The present investigation attempts to synthesize in situ spinel alumina castables fabricated by hydrous spinel gel prepared by the cost effective precursors via the rapid coprecipitation technique. The evolved gel phase has been categorically characterized and then added to a low cement castable batch [18-24] in different concentrations. The properties of such castable changing with temperature had been studied to analyze the feasibility of application of this gel bond to generate in situ spinel in the castable matrix. The micro structural features were also examined to elucidate the high temperature behavior of the same castable.

EXPERIMENTAL

The composition of the original spinel free castable is shown in table 1. The hydrated spinel gel was prepared via a novel coprecipitation method performed at a temperature below 10°C in the pH range 9.0-9.5 with a very rapid rate of precipitation. The differential thermal

analysis, thermogravimetric analysis (by Netzsch model) and particle size distribution test (by Malvern Mastersizer model) of the gel have been performed. This gel was very close in composition to the 1:1 stoichiometric ratio with solid content around 3.3 wt.% as determined by the simple ignition method; such remarkably high loss of ignition has also been reported in literature [27,28]. The x-ray diffraction and infrared spectroscopy patterns of the gel heated to different temperatures were also noted. The amount of the gel in a 100 wt.% castable batch was gradually increased from 0.5 to 4.0 wt.% to prepare in situ spinel castable. The batch material with requisite amount of deflocculant, water and gel was cast in cube moulds (25.4 mm), gently tamped by hand so that no vibration was needed [4] from out side. After scheduled curing and drying stages in moist atmosphere, dry air and oven [20-24] the samples were fired at 110, 900, 1200 and 1500°C with a soaking for two hours. The spinel castables were designated as AS, BS, CS and DS where A, B, C, D stood for 0.5, 1.0, 2.0 and 4.0 wt.% hydrated gel (code S) respectively.

The properties of such kind of castables were compared in respect of the increase of both the concentration of the gel mass and firing temperatures. Apparent porosity (AP), bulk density (BD) and cold crushing strength (CCS) of the castables were determined by the standard methods reported earlier [18-24]. The IR traces were obtained by using the instrument Perkin Elmer model (by KBr method) and the XRD (powder diffraction pattern) by the instrument "Philips Analytical" (model) with Ni filtrated Cu K_{α} at 40 KV/20 mA. Some selected samples were subjected to scanning electron microscope (SEM) study by the instrument JEOL JSM 5200 model; the EDS facility was utilized to identify the composition of the selected region of the castable matrix.

Table 1. Batch composition of original spinel-free castable and its selected properties after 1500°C.

Constituents	Amount (wt.%)
Aggregate (White fused alumina: coarse, medium and fine)	75.0
Matrix (Microsilica, micronized reactive alumina, refractory cement)	25.0
TOTAL	100
Properties	
Bulk density (gm/cm ³)	2.96
Apparent porosity (%)	15.2
Cold crushing strength (kg/cm ²)	1325
Flexural strength (kg/cm ²)	297

RESULTS AND DISCUSSION

Properties of hydrated magnesium aluminate gel

It is observed from figure 1 that the coprecipitated gel has an average particle size 19 micron with high surface area which might assist in situ spinellisation more rapidly than the solid state sintering when used in castable matrix. However Samaddar et al [27,28] reported that the particle size can be controlled to more fine region with tremendously high surface area (400 m²/g) if the unwanted agglomeration of particles is prevented during fast precipitation. This reactive gel promotes spinel formation as low as 900°C as evident from XRD pattern (figure 2a), but the additional phases also present in the material may be due to uncontrolled agglomeration during synthesis of the precursor. It has been confirmed later by the IR patterns. The XRD report at 1200°C (figure 2b) reveals the evolution of spinel phase prominently, although some corundum and periclase phase are very much clear in the figure. It may be suggested that the process parameters of this modified coprecipitation technique (e.g. stirring rate, surface active agent, pH and temperature) should be controlled rigorously to reduce those undesirable phases. The DTA and TGA traces (figure 3a and b) combinedly corroborate the generation of a lot of secondary phases and elimination of excessive volatile matters below 1000°C. Besides the removal of adsorbed water, sharp weight losses are quite clear between the temperature ranges 150-300°C and 400-530°C due to the structural breakdown of hydrous gel material. The changing trend of IR patterns of the coprecipitate calcined at 110, 700 and 900°C (figure 4a, b and c respectively) again suggest the necessity of tuning the process parameters of this rapid chemical route to upgrade the quality of this gel before mixing it in the castable batch. The IR pattern [29] at 110°C indicates the formation of double hydroxide (618 cm⁻¹) but the peaks at 1150 and 3280 cm⁻¹ show the evolution of Al-OH linkage may be due to uncontrolled formation of boehmite and gibbsite. Apart

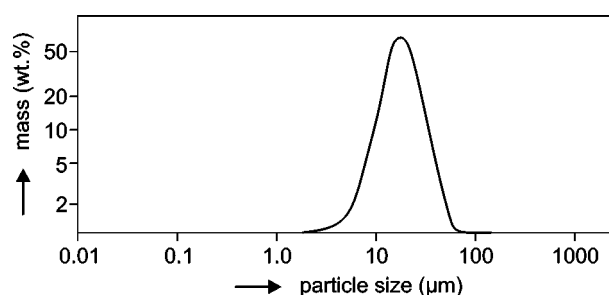


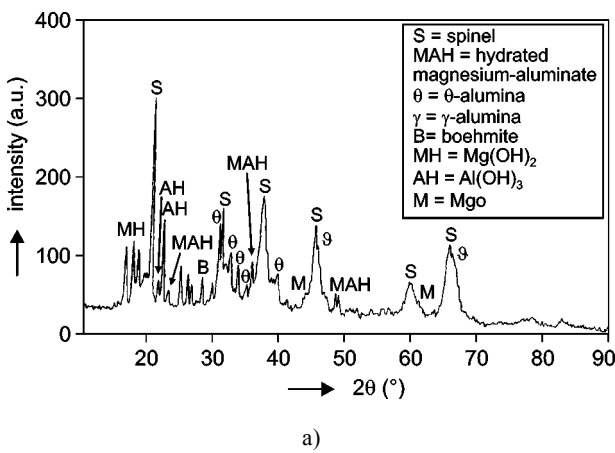
Figure 1. Particle size distribution curve of rapidly coprecipitated hydrated spinel.

from the presence of (OH) groups (at 3500, 2360 and 1656 cm^{-1}), a lot of entrapped amine and nitrates (1090, 1430 cm^{-1}) once again indicate [30] the unleashed rate of precipitation. Formation of spinel can not be asserted at 700°C (figure 4b), which becomes prominent at 900°C (613-697 cm^{-1} , figure 4c), still with the presence of OH, C=O and NH_2 groups. Consequently the precursor gel assumes very low solid content after calcinations might be due to the release of an extensive amount of H_2O , CO_2 and NH_3 as volatiles.

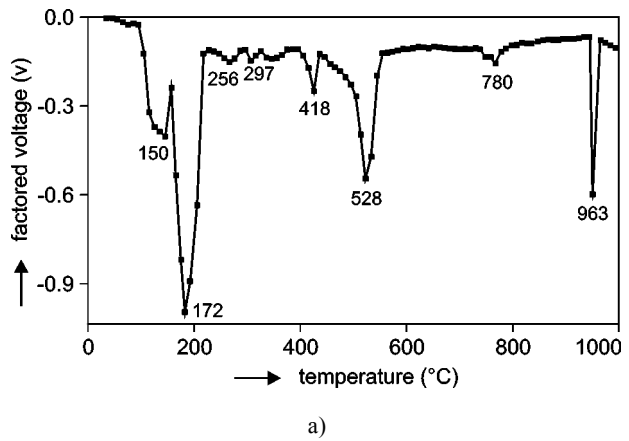
Properties of gel bonded castable

The properties of hydrated spinel bonded castable (with increasing temperature) have been evaluated in terms of BD, AP and CCS as shown in figure 5. It is apparent that the general trend of fall in properties within the intermediate temperature range (900-1200°C) remains the same when the concentration of gel additive has been changed from 0.5-4.0 wt.%. It is a common feature of high alumina cement bonded castable to

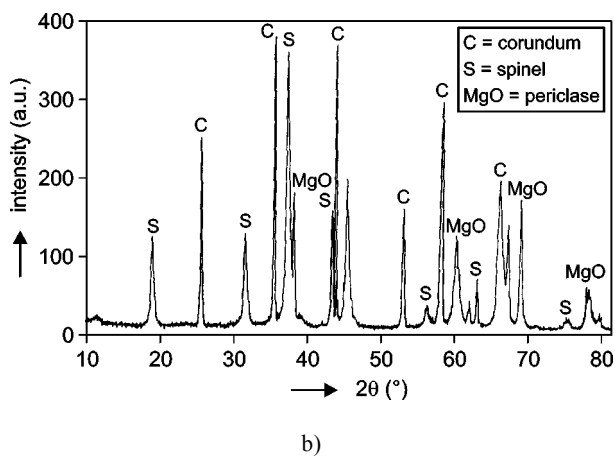
degrade within that temperature range due to complete dehydration of cement [31]. Beyond 1200°C the properties have been improved due possibly to the progressive densification in castable with ceramic bond formation. It is evident from this figure that the properties of CS type castable are the best among the four varieties. As we move from AS to DS composition, it is obvious that the castables are enriched with higher amount of solid gel fines. However when the concentration is increased from 0.5 to 1.0 wt.%, a drop in BD and CCS and a rise in AP up to 1000°C are very much conspicuous. This may be due to the significant volume stress rendered during in situ spinel formation [20-24, 32] in castable that generated a lot of flaws in the BS type. Nevertheless after 1200°C this fall is somewhat compensated by higher pinch of solid spinel present in BS than AS. When the concentration of coprecipitated gel is further increased to 2.0 wt.% (CS) the properties has reached the most satisfactory level as confirmed by the same figure. It is proposed that the volume stress in CS is offset by the homogeneous distribution of more spinel particles that efficiently increased the packing density of



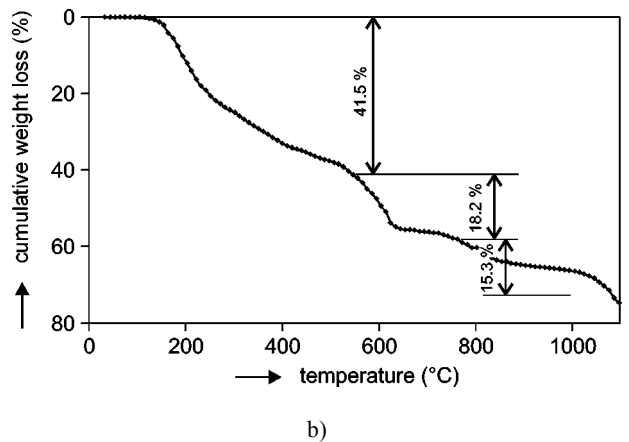
a)



a)



b)



b)

Figure 2. XRD pattern of the calcined gel at a) 900°C and b) 1200°C.

Figure 3. DTA (a) and TGA (b) traces of precursor gel.

the same castable. Moreover the continuous three dimensional network of the gel encapsulates the fused alumina aggregates to yield a denser microstructure. With due course of firing, this bond usually gives rise to the desi-rable $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ phase that holds the structure with an interconnected network [33]. At about 1400°C , another desirable phase $\text{CaO}\cdot 6\text{Al}_2\text{O}_3$ (hibonite), has been confirmed by the corresponding XRD pattern (figure 6) along with the spinel and corundum crystals. The interlocking platy crystals of hibonite [33, 34] firmly bond the matrix and grains to improve the physical properties (figure 5) of the CS type castable. However some low melting phases has also been found (as discussed later) because of a higher amount (5.0 wt.%) of micro silica present in the original batch (table 1). Such low melting C-A-S phases (of the ternary system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$) adversely affect the hot

properties of the castable [20]. For this reason the microfine silica should be optimized below a certain limit in the spinel-alumina castable [35]. The enormous porosity in four types of castables possibly arises due to a substantial amount of volatiles released from the hydrated gel with increasing temperature as mentioned

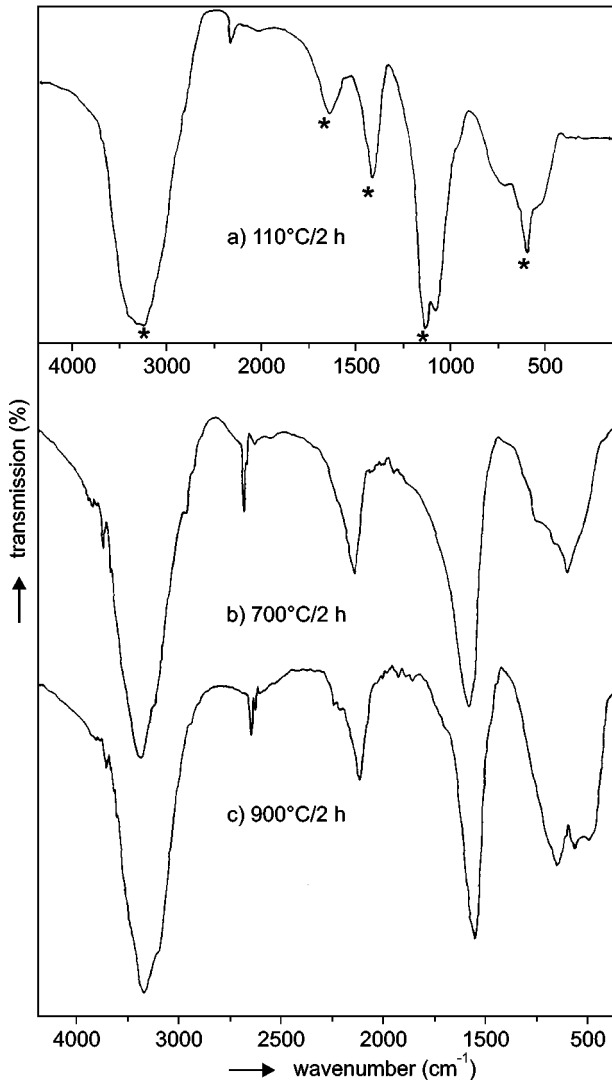


Figure 4. IR spectra of the spinel gel calcined at a) 110°C , b) 700°C and c) 900°C .

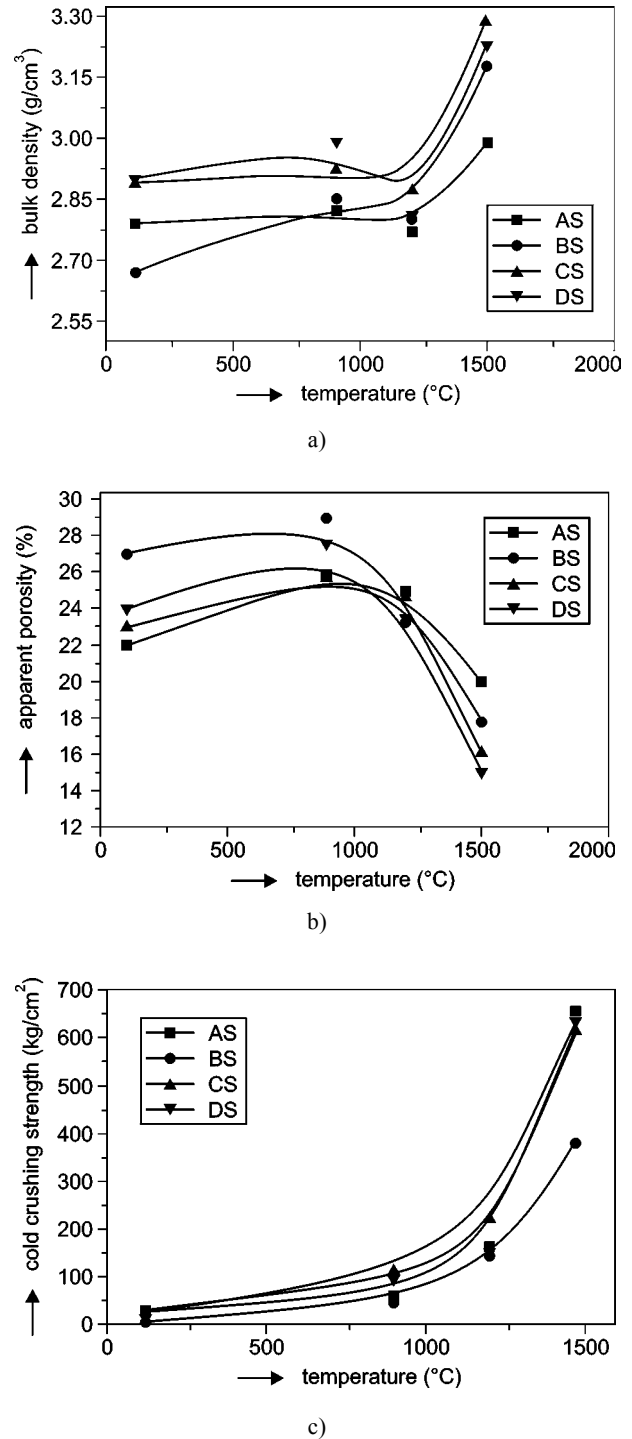


Figure 5. Variation of a) BD, b) AP and c) CCS of AS, BS, CS and DS castables with increasing temperature.

in the DTA and TGA reports earlier. Finally, when the gel concentration is increased to 4.0 wt.% (DS type), the drop in properties again takes places. As the amount of gel is maximum here it may be anticipated that the volume stress in castable is also maximum here to generate sporadic cracks in them. Secondly it is reported in literature that when the concentration of gel additive in castable is increased beyond a certain limit it causes a rapid fall in green strength and problem in installation [36,37]. As the migration of finer particles of gel in castable is too high and the amount of fugitives present is also the largest, therefore the performance of DS type castable is seriously deteriorated. All these features are corroborated again when figure 7 is observed. They strongly suggest that the concentration of the co-precipitated gel should be kept to 2.0 wt.% in this castable to exploit the better properties.

Figure 8 shows the SEM micrographs (with an EDS trace) of the spinel-bonded castable after being fired at 1500°C. Apart from the corundum and hibonite crystal, small spinel grains and scattered low melting (CaO-Al₂O₃-SiO₂) phases exist in the microstructure. Some cracks are also visible which have possibly been generated by the mismatch of thermal expansion coefficient of that glassy phase with the other crystalline parts. Large volume expansion during spinellisation also might lead to such sporadic cracks. The micro silica content of the batch should also be minimized to reduce that glassy phase.

CONCLUSIONS

From the present work it may be concluded that high alumina based in situ spinel alumina castable can be conveniently fabricated by the spinel gel synthesized via a rapid co precipitation technique. That agglomera-

ted hydrous gel need to be beneficiated further by minimizing the undesirable secondary phases by proper optimization of the process parameters of the chemical route. The physical properties of the respective castable are the best when the concentration of the gel mass is 2.0 wt.%. This spinel forming reaction together with the

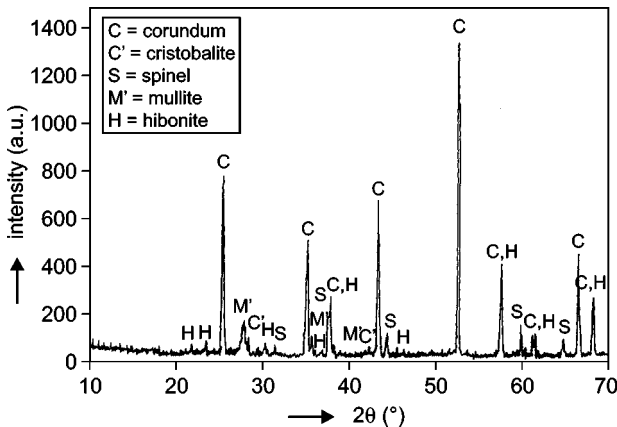
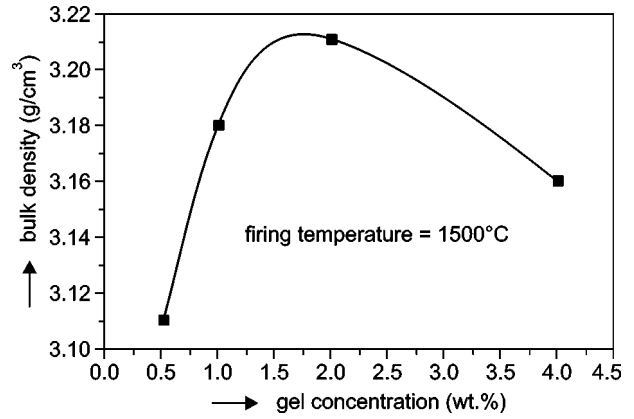
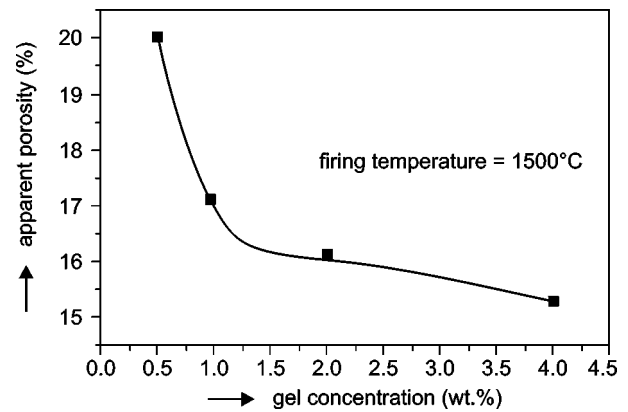


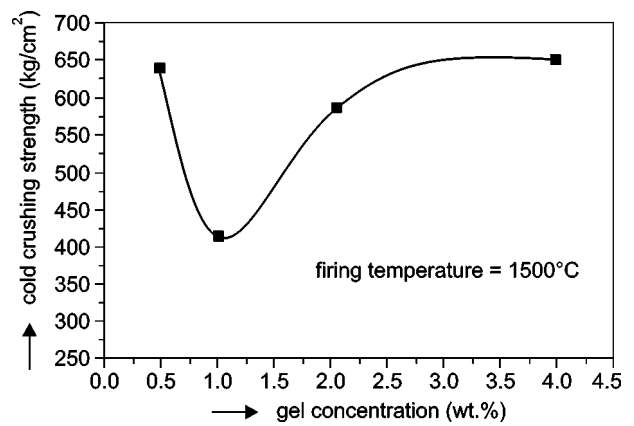
Figure 6. XRD pattern of CS type castable after firing at 1500°C.



a)

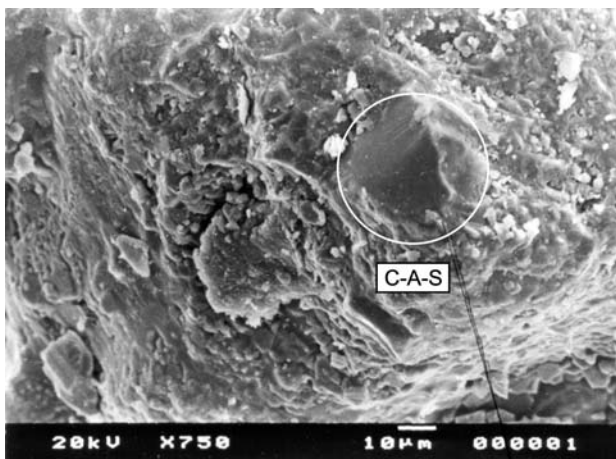


b)

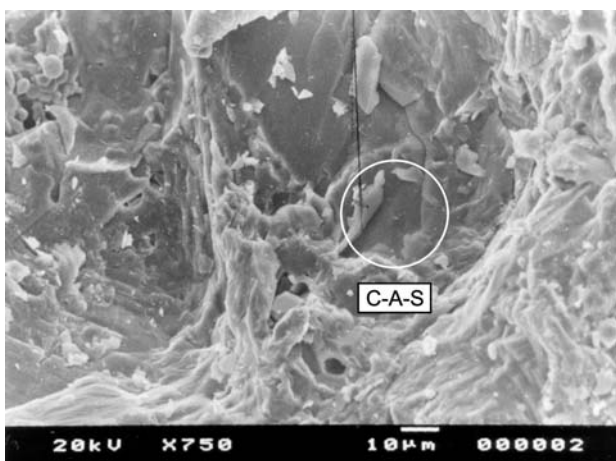


c)

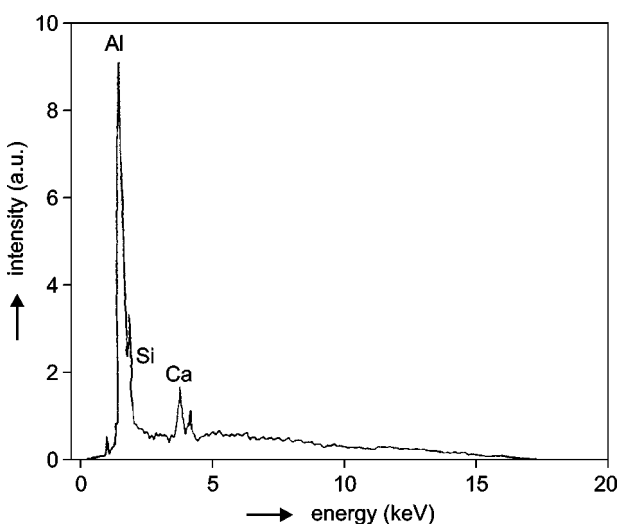
Figure 7. Variation of a) BD, b) AP and c) CCS with increasing spinel concentration in castables fired at 1500°C.



a)



b)



c)

Figure 8. Micrographs (a, b) of CS castables fired at 1500°C with the selective EDS pattern (c).

release of volatile materials from the gel, however, leads to serious damage in some castable specimens. If the microsilica content of the original batch is kept at minimum level the detrimental low melting phases in the matrix can be avoided.

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References

1. Nishio, H. in: Proc. of UNITECR, p. 2-3, Osaka, Japan 2003.
2. Banerjee S.: Am.Ceram.Soc.Bull. 77, 59 (1998).
3. Studart A.R. et al.: Am.Ceram.Soc.Bull. 78, 65 (1999).
4. Kang H.S. et al. in: Proc. of UNITECR, p. 264-71, Kyoto, Japan 1995.
5. Jones V.: Ceramic Industry 148, 49 (1998).
6. Wohremeyer C. et al. in: Proc. of UNITECR, p. 647, Osaka, Japan 2003.
7. Studart A.R. et al.: Am.Ceram.Soc.Bull. 81, 32 (2002).
8. Mukhopadhyay S. et al.: Ceramic International 29, 671 (2003).
9. Mukhopadhyay S. et al.: Industrial Ceramics 20, 82 (2000).
10. Mukhopadhyay S. et al.: Trans. Indian Ceram.Soc. 62, 106 (2003).
11. Mukhopadhyay S. et al.: Ceramic International 28, 719 (2003).
12. Kato H. et al.: Taikabutsu overseas 16, 22 (1996).
13. Mori H. et al. in: Proc. of UNITECR, p. 171-178, Kyoto, Japan 1995.
14. De H., Ping L. in: Proc. of UNITECR, p. 247- 251, New Orleans, USA 1997.
15. Madias J. et al.: Interceram 49, 348 (2000).
16. Fuhrer M. et al.: J.Euro.Ceram.Soc. 18, 813 (1998).
17. Korgul P. et al.: J.Euro.Ceram.Soc. 17, 77 (1997).
18. Mukhopadhyay S. et al.: Ceramic International 29, 857 (2003).
19. Mukhopadhyay S. et al.: Interceram 51, 282 (2002).
20. Mukhopadhyay S. et al.: Ceramic International 30, 369 (2004).
21. Mukhopadhyay S. et al.: Industrial Ceramics 24, 199 (2004).
22. Mukhopadhyay S. et al.: Industrial Ceramics 23, 198 (2003).
23. Mukhopadhyay S. et al.: Industrial Ceramics 24, 33 (2004).
24. Mukhopadhyay S. et al.: Proc. of UNITECR, p. 158-161, Osaka, Japan 2003.
25. Dev Sikdar J. C. : J.Materials.Sci. 20, 4454 (1985).

26. Bratton R. J.: *Am.Ceram.Soc.Bull* 48, 62(1969).
27. Samaddar B. N. et al.: *Trans. Indian Ceram.Soc.* 25, 33 (1966).
28. Samaddar B. N., et al.: *J.Am.Ceram.Soc.* 61, 279 (1978).
29. Mukhopadhyay S. et al.: *Ceramics International* 31, 333 (2005).
30. Smith B.: *Interpretation of IR spectra, A Systematic Approach*, CRC Press 1999.
31. Parker K. M. et al.: *Trans. and J.Brit.Ceram.* 81, 35 (1982).
32. Hwang K.H. et al. in: *Proc. of UNITECR*, p. 1575, New Orleans, USA 1997.
33. Simonin F. et al.: *J.Am.Ceram.Soc.* 83, 2481 (2000).
34. Khalil N. M. et al.: *Trans. and J.Brit.Ceram.* 100, 110 (2001).
35. Ko Y. C. in: *Proc. of UNITECR*, p.22, Berlin, Germany 1999.
36. Pandolfelli V. C. et al.: *Am.Ceram.Soc.Bull.* 81, 41 (2002).
37. Mukhopadhyay S. et al: *Ceramics-Silikáty* 48, 100 (2004).

VLASTNOSTI ODLÉVATELNÝCH HMOT S NÍZKÝM
OBSAHEM CEMENTU OBSAHUJÍCÍ CHEMICKY
PŘIPRAVENÝ HYDRATOVANÝ SPINEL

SUNANDA MUKHOPADHYAY, TARAK NATH SEN,
SK. MOMBASSAR HASSAN, PANCHUGOPAL PAL

*College of Ceramic Technology, 73 A. C. Banerjee Lane,
Kolkata - 700010, India*

Prekurzor gelu hlinitanu křemičitého byl syntetizován rychlou koprecipitační technikou při poměrně nízké teplotě. Z tohoto gelu je možné připravit spinel při podstatně nižších teplotách než při slinování pevné fáze. Při vyšších teplotách je tvorba spinelu ovšem spojena s tvorbou dalších fází, jako je korund a periklas. Připravený gel byl v koncentraci 0,4 až 0,5 hmot.% přidán k vysoce hlinité odlévatelné hmotě k přípravě spinelohlinitých monolitických žáromateriálů. Některé nekontrolovatelná aglomerace a vysoký obsah OH, NH₂ a C=O skupin v prekurzoru gelu přináší obavy o použitelnost připravené odlévatelné hmoty. Nicméně optimální přídavek 2 hmot.% gelu sehraje dostatečnou roli s ohledem na fyzikální vlastnosti materiálu. K potlačení nežádoucí tvorby CaO-Al₂O₃-SiO₂ fáze v matrici je však nutné snížení obsahu mikročástic SiO₂.