

Physico-chemical investigations on the sintering behaviour of red mud - flue dust composites

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ABSTRACT

Two industrial waste products namely red mud and flue dust have been utilised to form composites and their sintering behaviour was investigated in this study. It has been observed that red mud alone can be sintered around 1250°C. Addition of flue dust can reduce the sintering temperature and bring it in the range of 1150 - 1200°C depending on the extent of flue dust addition (10-30%). The sintering kinetics initially follows the Johnson - Mehl model of nucleation and grain growth and subsequently beyond fractional conversion of 0.7, follows the three dimensional contracting geometry model. XRD studies reveal that there are at least 6-8 phases in the sintered product. Some of these are Fe_2O_3 , $Ca_3Fe_2Si_3O_{12}$, SiO_2 , $NaAlSiO_4$, $FeTiO_3$, TiO_2 and $Na_2Si_2O_5$. EPMA studies show that apart from the above phases, smaller amounts of $ZrSiO_4$ and a few other rare earth compounds were also present in the sintered product. The silicate phases are essentially present in the grain boundaries of other non-silicate phases and these phases are responsible for reduction in the sintering temperature. These glassy phases are also responsible for inter-particle bonding in the composites. This conclusion has also been verified through scanning electron microscopy (SEM). The sintering temperature and fraction of the flue dust in the composites have been optimised at 1200°C and 20% respectively.

Key words : Red mud, Sintering dust, Composite, Ceramic tiles.

INTRODUCTION

Aluminium is the most abundant metallic element in the earth's crust. It is normally found combined with other elements, and does not occur in its pure

state. It appears in a wide variety of minerals combined with oxygen, silicon, the alkali and alkaline earth metals. It is also available as hydroxides, sulphates and phosphates. Aluminium is produced industrially by the Hall-Heroult process in which alumina is fused with the help of cryolite and the molten alumina is electrolysed using carbon electrodes. The primary raw material for the process is alumina and is produced by a process called the Bayer process. The solid residue generated from the Bayer process is called red mud which is highly alkaline ($\text{pH} = 10-12$) and creates substantial environmental hazards. Hence its safe disposal and utilisation pose a major scientific challenge.

The most important environmental problem in the Bayer process is the disposal of the red mud. The solution left with the residue after an economical amount of washing is still very alkaline and can not be allowed to contaminate the ground water. An aqueous slurry of the residue that had been washed with 1000 times its mass of distilled water still reached a pH value of 10.5 on standing. The fine residue, even after years of consolidation, does not have enough strength to support buildings or equipment. These properties make disposal of red mud a difficult problem. In many places disposal was done to a marine environment where the alkalinity was diluted by large quantities of water. This method has been employed in Europe and Japan where the disposal was done at sea and in US where disposal was done in the river. Inland refineries simply used a convenient valley or built retaining dikes on flat land to form residue disposal areas. In some cases, the sandy portion of the residue was used to build the dikes. This method can be effective and cheap if care is taken to protect the surroundings by proper sealing techniques^[1,2].

Many investigations have been directed towards finding a commercial use of red mud. The high iron content of some red mud suggested production of pig iron. Similarly, chemical processes have been developed for the recovery of Al_2O_3 , V_2O_5 , Na_2O and TiO_2 from red mud. Although all are technically possible, none were found to be economically viable. Small quantities of red mud have also been used in making Portland cement. Since the red mud is clay-like, it can be used as raw materials for ceramic materials. The sodium causes formation of low melting point glasses around 1450K, giving a vitreous bond. Bricks have been made commercially, but economic factors and other shortcomings of the bricks have eliminated this use.

CERAMIC TILES FROM RED MUD

Manufacture of ceramic products such as tiles from red mud are also an attractive proposition since it contains several of the required ingredients. Various investigators have studied the techniques for producing ceramic tiles from red mud. Puskas^[3] prepared ceramic wall tiles from a mixture of red mud, min-

erals and/or silicate containing materials. Shiyanskaya^[4] also studied the possibility of using red mud for production of ceramic tiles. By changing the various process parameters, different types of tiles were obtained. Rudolf^[5] patented a process for the preparation of ceramic tiles from red mud mixed with household refuse and consumed fuller's earth. It was stated that household refuse and consumed fuller's earth are very good source of energy which is more than that required for firing of ceramic products. Tanaka and associates^[6] provided a number of choices for additives to be mixed with red mud towards the preparation of ceramic products. These additives were granulated or slowly cooled furnace slag, converter slag, glass powder, plastic clay, alkali compounds such as fluorides and/or borides to be used in specific weight ratios. A comprehensive summary of the work carried out by various investigators in this area have been provided by Thakur and Das^[1]. In this study, we have investigated the implication of using flue dust, a major waste material from the thermal power plants, as an additive to red mud in making ceramic tiles. Since tile making involves sintering of red mud - flue dust mixtures, it is necessary to have a thorough scientific understanding of the sintering process.

However, many of the key scientific issues in relation to tile preparation from red mud have not been addressed by the above investigators. Some of these question are : What are the equilibrium phases that are formed during the sintering of red mud - flue dust mixtures? What kinetic laws govern the sintering process? What complex mineral phases are formed during sintering? What are the bonding mechanism involved during the tile making process? This paper attempts to answer some of these questions.

EXPERIMENTAL

Materials

The sintering characteristics of the red mud - flue dust mixtures were carried out using a red mud sample obtained from the Alcan Chemicals plant at Burnt Island, Scotland, UK. The flue dust sample has been collected from one of the thermal power plants of M/s Calcutta Electric Supply Company (CESC), Calcutta. The chemical compositions of the red mud and flue dust are given in Table 1.

Procedure

The red mud was dried in an air oven at 110°C for 4 hours. The dried red mud was then ground in a mortar-pestle and sieved through 100 mesh. The sieved powder was then thoroughly mixed with flue dust (10, 20 and 30% by mass in separate batches) in an agate mortar. The red mud - flue dust mixtures were then compacted using an organic binder to produce tile specimens of diameter 22 mm and thickness 5-7 mm. The specimens were then slowly dried for 7-

8 hours in an air oven maintained at 80°C. The dried specimens were then heated to different temperatures i.e. 1150° 1200° and 1250°C in an electric resistance furnace provided with a programmable temperature controller at a heating rate of 5°C/min. After attaining the final temperature, the samples were kept at that temperature for a period of 30 minutes and allowed to cool inside the furnace.

Table - 1 : Compositions of red mud and flue dust (in mass percent)

Red mud		Flue dust	
Constituents	Composition %	Constituents	Composition %
Fe ₂ O ₃	46	Fe ₂ O ₃	3.2
Al ₂ O ₃	20	SiO ₂	59.9
TiO ₂	6	Al ₂ O ₃	29.2
SiO ₂	5	TiO ₂	2.7
Na ₂ O	4	Alkaline oxides	0.3
K ₂ O	1	Alkaline earth Oxides	3.1
CaO	1	P ₂ O ₅	1.4
MgO	1	Others	0.2
LOI	10		
Others	6		

The sintered samples were analysed using X-ray diffraction (XRD), scanning electron microscopy (SEM) and electron probe micro-analysis (EPMA) techniques to gain detailed insight into the sintering of red mud - flue dust mixtures.

To investigate the kinetic laws governing the sintering process, non-isothermal thermogravimetric technique was employed. A Netzsch STA 409C model thermal analyser was used. The experiment was carried out with -100 mesh red mud powder mixed with flue dust sample. Sintering properties of only red mud was also investigated. The average surface area of red mud sample is 9.75 m²/g. The sample mass used for thermal analysis studies was about 45 mg. Such fine grain size was used to obtain a representative sample while conducting experiments with small quantities. Static air was used as the sintering medium. In the experiments alumina was used as the reference material. The maximum temperature was kept at 1270°C and the heating rate was chosen at 10°C per min. Extensive studies were carried out with red mud and red mud - flue dust mixtures. From the data generated, the kinetic mechanisms for the sintering of red mud - flue dust mixtures were elucidated and the major kinetic parameters were calculated.

RESULTS AND DISCUSSION

Elucidation of Mechanism of Sintering

Sintering is a complex process and specially in situations where red mud and flue dust mixtures are being sintered. In view of the above, the weight loss taking place during sintering process could not be attributed to one single reaction but a series of complex reactions. In the present analysis, the fractional conversion (α) during sintering is defined as the ratio of weight loss during sintering at any time t and maximum weight loss recorded during the sintering process. Figure 1 presents the primary kinetic plots (α vs t) obtained from the continuously recorded weight loss data during the non-isothermal sintering of red mud and red mud - flue dust mixtures. It may be noted that there is little change in the α - t plot after the addition of 10% flue dust in the red mud (Fig. 1) and at the end of the run, the α - t plot flattens out.

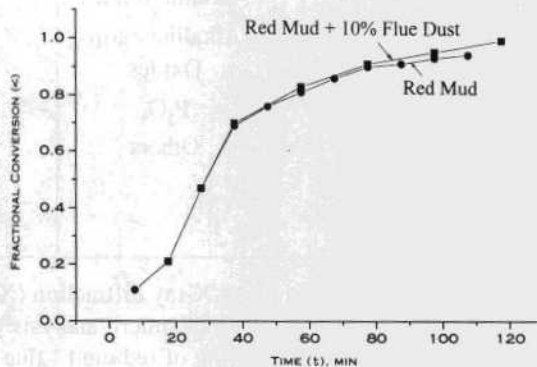


Fig. 1 : Primary kinetic plots for sintering of red mud and red mud - flue dust mixtures

To check the kinetic model(s) followed by the sintering process, the technique provided by the reduced time plots were used. To obtain the reduced time plots, the following procedure is adopted.

The normal kinetic relationships are expressed in the form :

$$G(\alpha) = kt \quad \dots(1)$$

If $t_{0.5}$ is the time required to obtain 0.5 fraction reacted, i.e. when $\alpha = 0.5$ then

$$G(\alpha)_{\alpha=0.5} = kt_{0.5} \quad \dots(2)$$

Dividing Eq. (1) by Eq. (2), one obtains the kinetic relationship in an altered form given as :

$$G(\alpha) = [G(\alpha)_{\alpha=0.5}].(t/t_{0.5}) \quad \dots(3)$$

Eq. (3) is independent of the kinetic rate constant and is dimensionless. Thus for a particular reaction mechanism, a single equation of this type represents all kinetic data irrespective of the nature of system, temperature and other factors which affect the reaction rate. Each mechanism, therefore, has an unique reduced time plot. Use of such plots have been previously reported in the literature^[7-11]. Here $t_{0.5}$ has been chosen because α has crossed a value of 0.5 in both experiments. The same approach can be used employing other time values. The value of $t_{0.5}$ has been calculated from the α -t plots and the corresponding $(t/t_{0.5})$ are calculated. Master plots of various mechanisms are obtained by plotting α against the calculated values of $(t/t_{0.5})$. Reduced time plots for the experimental data are then superimposed on the theoretical plots to determine the kinetic law governing the sintering of red mud - flue dust mixtures. Fig. 2 presents the experimental points superimposed on the theoretical reduced time plots. It is observed that the data conforms well with the Johnson - Mehl equation up to α value of about 0.7. Subsequently the mechanism shifts to the 3-D contracting geometry model. It is also observed that with addition of 10% flue dust in red mud, there is no appreciable change in the rate law governing the sintering process (Fig. 3).

Thus the rate laws governing the sintering of red mud and red mud - flue dust mixtures may be expressed as :

$$(d\alpha/dt) = k.t.(1-\alpha) \quad \dots(4) \quad \left| \begin{array}{l} \text{[For } \alpha = 0-0.7] \end{array} \right.$$

which on integration gives :

$$[-\ln(1-\alpha)]^{1/2} = k.t \quad \dots(5)$$

$$\text{and } (d\alpha/dt) = k.(1-\alpha)^{2/3} \quad \dots(6) \quad \left| \begin{array}{l} \text{[For } \alpha > 0.7] \end{array} \right.$$

which on integration gives :

$$[1 - (1-\alpha)^{1/3}] = k.t \quad \dots(7)$$

The above analyses indicate that the sintering process is initially controlled by nucleation and grain growth and beyond 70% completion follows the three dimensional contracting geometry model i.e. the process is governed by three dimensional movement of the reaction interface.

Eq. (4) may be re-written as :

$$(d\alpha/dt) = A. \exp(-E/RT).t.(1-\alpha) \quad \dots(8)$$

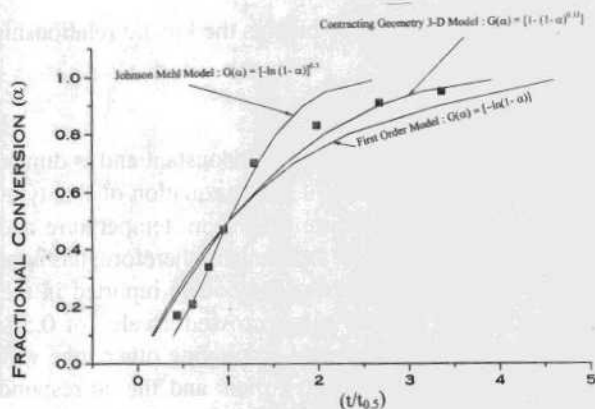


Fig. 2: Reduced time plot for sintering of red mud

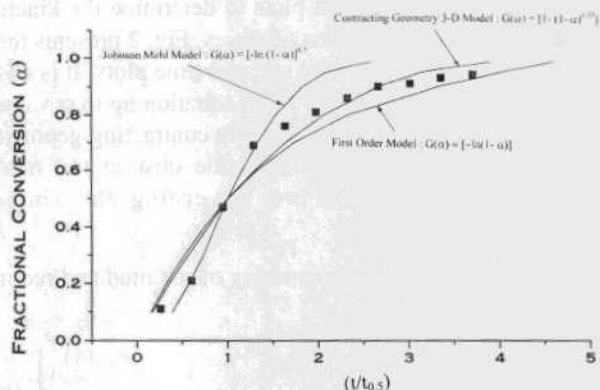


Fig. 3: Reduced time plot for sintering of red mud - 10% flue dust mixture

The integral approach used by Ray & Dixit^[12] has been used for the calculation of activation energy (ΔE). The pre-exponential factor (A) was determined using the following expression :

$$A = G(\alpha) / \int_0^1 \exp(\Delta E/RT).dt \quad \dots(9)$$

Figs. 4 and 5 presents the Ray & Dixit plots for sintering of red mud and red mud - 10% flue dust mixtures. The ΔE and A values are listed in Table 2.

After obtaining the mechanism of sintering through the thermal analysis studies, efforts were made to understand the various phases formed and the mechanism of bonding during the sintering of red mud - flue dust tile specimens. These findings are summarised below.

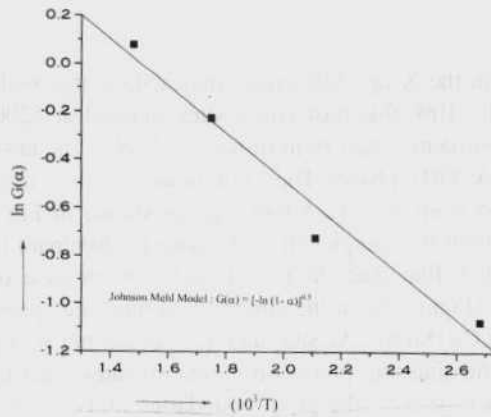


Fig. 4: Dixit & Ray plot for sintering of red mud - 10% flue dust mixture for α values upto 0.7 (Controlling mechanism : Johnson Mehl Model)

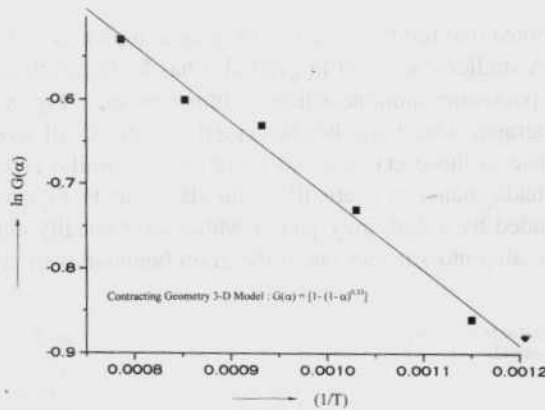


Fig. 5: Dixit & Ray plot for sintering of red mud - 10% flue dust mixture for α values beyond 0.7 (Controlling mechanism : 3D Contracting Geometry Model)

Table 2 : Summary of activation energy (ΔE) and pre-exponential factor (A) values for sintering of red mud - flue dust mixtures

Temperature Range (K)	Rate Controlling Equation	E (kJ/g.mol)	A
373-673	$(d\alpha/dt) = A \cdot \exp(\Delta E/RT) \cdot t \cdot (1-\alpha)$	8.1	0.21
873-1273	$(d\alpha/dt) = A \cdot \exp(\Delta E/RT) \cdot (1-\alpha)^{2/3}$	7.3	0.21

XRD Studies

The results from the X-ray diffraction studies show that both unsintered red mud and red mud - 10% flue dust composites sintered at 1200°C have Fe_2O_3 phase as main constituent. Apart from different silicates, the unsintered red mud has $\text{FeO}(\text{OH})$ and $\text{Al}(\text{OH})_3$ phases. The amorphous behaviour of these phases can easily be identified from the line broadening as shown in Fig. 6. The FeTiO_3 phase is found in both the samples but it is more predominant in the tile specimen containing 10% flue dust. SiO_2 is found only in case of the flue dust containing sample (Figure 7). In the sintered red mud tile specimen, the minor phases such as $\text{Na}_2\text{Ca}_3(\text{SiO}_3)_3$, Al_2SiO_5 and TiO_2 could not be found. This indicates that during the sintering process different silicates react together to form other silicates which goes to the grain boundaries of Fe_2O_3 , FeTiO_3 and SiO_2 phases.

EPMA Studies

It may be noted that red mud itself is a highly complex system having several phases. EPMA studies show that in general it has Fe_2O_3 , alumino-silicates such as calcium or potassium alumino-silicates, illmenite, etc. Fig. 8 represents one of such micrograph, where the bright crystals scattered all over the area are Fe_2O_3 (A). Close to those crystals and more or less similar type of crystals of little darker shade than Fe_2O_3 are illmenite (B). The Fe_2O_3 and illmenite are mostly surrounded by a dark grey phase, which are basically alumino-silicates. In other words, alumino-silicates are at the grain boundaries of crystalline Fe_2O_3 .

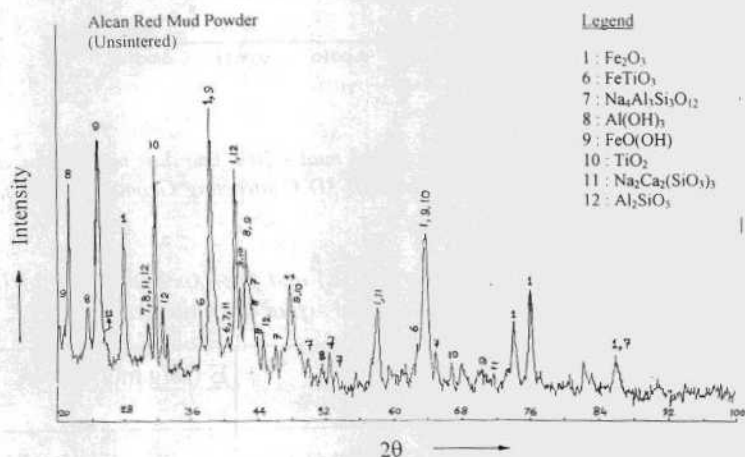


Fig. 6 : XRD pattern for unsintered red mud from Alcan

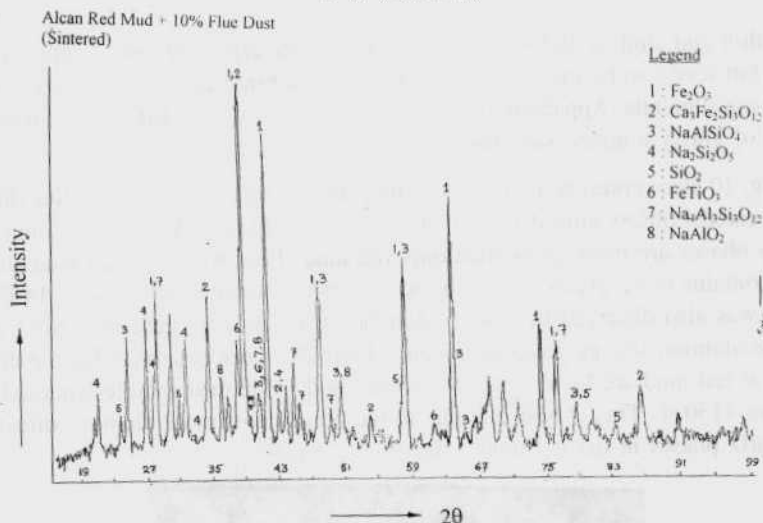


Fig. 7 : XRD pattern for sintered tiles containing Alcan red mud and 10% flue dust

and ilmenite phases and are responsible for bonding amongst various phases. It has also been found that alumino-silicates are agglomerated in one or two places. In the same micrograph the big grey needle like area contains alumino-silicate with little Na and Ti (C).

In red mud, free quartz or silica was not found. Whereas, in case of the sample containing red mud - 30% flue dust, there are many quartz particles present (Fig. 9). The darkest grey areas are the quartz phase. Around the quartz phases alumino-silicates are also present with little potassium in it. This layer is

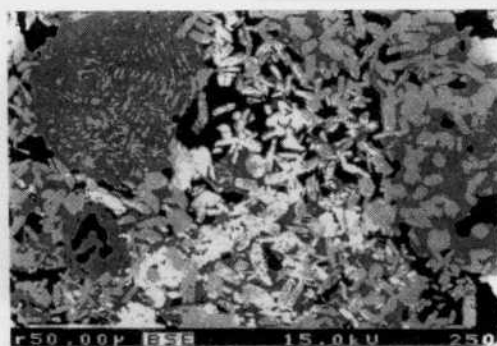


Fig. 8 : EPMA microphotograph showing various phases - Fe_2O_3 (A), ilmenite (B) and alumino-silicates containing little Na and Ti (C)

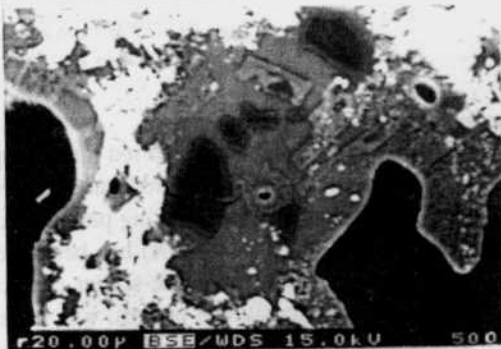


Fig. 9 : EPMA microphotograph showing Fe_2O_3 and ilmenite embedded in glassy alumino-silicates

very thin and slightly lighter in colour. Other grey areas are also aluminosilicates but seems to be melted. In this case also the brightest areas are Fe_2O_3 and some are illmenite. Apparently Fe_2O_3 or illmenite are embedded inside different types of glassy aluminosilicates.

Fig. 10 also represent a sintered sample containing red mud - 30% flue dust. After careful observation it is clear that in case of Figs. 9 & 10 the amount of glassy phases are much more than only red mud (Figs. 8). Since red mud - flue dust contains more glassy phases, its sintering temperature is also less. In Fig. 10, it was also observed that some blow holes which were generated from the molten aluminosilicate containing areas. It has also been observed that the densities of red mud are lower than that of red mud - flue dust samples sintered at 1100 or 1150°C. This is basically due to the presence of more aluminosilicates or quartz phases in the red mud - flue dust samples.

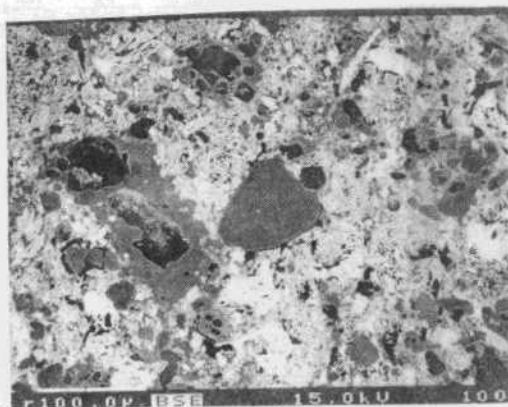


Fig. 10 : EPMA microphotograph showing blowholes generated in the glassy aluminosilicate phase

SEM Studies

In this study a sintered red mud composite containing 20% flue dust has been used. Sintering was carried out at different temperatures in the range of 1000-1200°C for different soaking periods. Scanning electron microscope (JEOL JSM 840A with KEVEX EDX) has been used for micro-structural evaluation of experimental samples. Back-scatter electron imaging (BSEI) was done for obtaining the compositional images, which usually gives the clear idea of the different phases. Elemental X-ray dot mapping was also done to correlate with the compositional images. Due to the instrumental limitations oxygen could be analysed, however, it was assumed that all the elements are present in the form of their oxides. XRD analysis of the sintered composite was also carried out to correlate with the SEM-EDX results.

Figs. 11 (A)-(D) shows the microstructures of red mud - 20% flue dust composite sintered at 1200°C. These are back-scatter electron images and are also known as compositional images. The contrast and the brightness of the images are related with the atomic number of different elements. Brighter area indicates the presence of higher atomic number elements such as iron and titanium and darker area indicates the lower atomic number elements such as sodium, silicon, aluminium and calcium in this case. Darkest area (black) represents porosity/void.

From Figs. 11 (A)-(D), it is clear that the distribution of all the phases are more or less uniform. The voids are mostly generated from the site where molten alumino-silicates are present. The different alumino-silicates are distributed through out the matrix uniformly. It may also be noted that the alumino-silicates have dual functions namely, controlling the porosity and contributing in the bonding

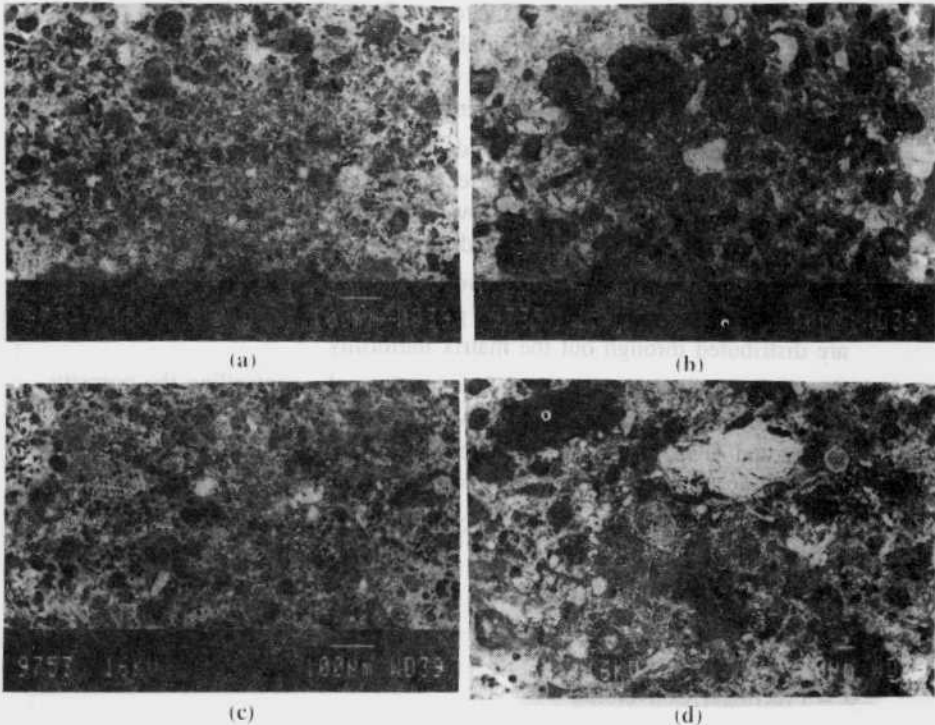


Fig. 11 (a)-(d) : Backscatter electron images of the red mud composites containing 20% flue dust sintered at 1200°C. Microstructures taken from different areas show more or less uniform distribution of various phases. Figures 11 (a) & (c) show uniform distribution of porosity (black areas) and major phases (Fe_2O_3) & TiO_2 - white area and SiO_2 and Al_2O_3 - darker area). Figures 11 (b) & (d) show location of voids near the alumino-silicates.

of various phases such as Fe_2O_3 , ilmenite, quartz and TiO_2 . Therefore, alumino-silicates are the main constituents for controlling the sintering behaviour of these composites. In view of the above, the properties of tailor made ceramic materials can be controlled by controlling the distribution and composition of alumino-silicates in the ceramic matrix.

CONCLUSION

- (1) The sintering of red mud and red mud flue dust composite samples follow the Johnson - Mehl kinetic rate law expressed as $(d\alpha/dt) = A.\exp(\Delta E/RT).t.(1-\alpha)$ up to a fractional conversion of 0.7. Subsequently, it follows the 3-D contracting geometry model expressed as $(d\alpha/dt) = A.\exp(\Delta E/RT).(1-\alpha)^{2/3}$.
- (2) The activation energy (ΔE) of the sintering process lies in the range of 7.3 - 8.1 kJ/mol and the pre-exponential factor (A) has been calculated as 0.21.
- (3) The X-ray diffraction studies indicate that Fe_2O_3 is the major phase present in the sintered sample. Quartz is only found in the sample containing flue dust. The other major phase present is FeTiO_3 . In addition various silicates and alumino-silicates are also present.
- (4) EPMA studies indicate that the flue dust containing sample has more glassy phase present and this glassy phase is responsible for bonding the other particles. This sample also has a lower sintering temperature as compared to the specimen containing only red mud.
- (5) The SEM studies indicate that the voids are mostly generated from the site where molten alumino-silicates are present. The different alumino-silicates are distributed through out the matrix uniformly.
- (6) The alumino-silicates have dual functions namely, controlling the porosity and contributing in the bonding of various phases such as Fe_2O_3 , ilmenite, quartz and TiO_2 . Therefore, alumino-silicates are the main constituents for controlling the sintering behaviour of these composites.

In view of the above, the properties of tailor made ceramic materials can be controlled by controlling the distribution and composition of alumino-silicates in the ceramic matrix.

SYMBOLS

α = Fractional Conversion

A = Pre-exponential factor

ΔE = Activation Energy (kJ/mol)

k = Rate constant (time^{-1})

t = Reaction time (min)

T = Temperature (K)

$f(\alpha)$, $G(\alpha)$ = Functional form of α

t_α = Time required to attain a fractional conversion α (min)

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