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COLD BONDED PELLETIZATION OF IRON ORE FINES AND LECO CHAR

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ABSTRACT

Cold bonding processes have been developed with a view to conserve energy in pellet hardening step. The incorporation of the reductant and fluxes in the pellet also ensures a blast furnace burden that is homogeneous with resultant smooth operations of the furnace. The present paper deals with the studies conducted on the production of composite iron ore pellets using iron ore fines, eco-char, hydrated lime and natural silica flour as well as rice husk silica. The results indicate that the composite pellets with rice husk has superior strength compared to the pellets with natural crystalline form of silica. Studies on $\text{CaO-H}_2\text{O}$ -rice husk silica reaction system revealed that a gel like calcium silicate hydrate (CSH-I) is formed during the steaming operation that is responsible for the strengthening of the composite pellet. The studies on the kinetics of the hydrothermal reaction revealed that the reaction is diffusion controlled and the product formed is calcium silicate hydrate. The reducibility studies indicated good reducibility with minimum swelling.

INTRODUCTION

The conventional method of heat hardening of iron ore pellets for iron production is an energy intensive and is associated with energy consumption of 1,50,000-2,50,000 KCal/tonne of pellets depending on the nature of the raw materials. Cold bonding processes have been developed with a view to conserve the energy requirements of the pellet hardening step. The incorporation of reductant and flux in the iron ore has the advantage of not only utilising carbonaceous fines but also in the production of a composite pellet with the iron oxides and the reductant in their natural states with neither reduction nor oxidation at relatively low hardening temperatures, characteristic of the process.

Incorporating a reductant inside the pellet invariably reduces the strength of the pellet particularly from the point of view of the very demanding conditions of the blast furnace. However with the use of composite pellets in small blast furnaces and low shaft furnaces, it is possible to produce foundry grade pig iron at competitive prices. This would also help to meet the regional requirements of pig iron for the foundry industry. In cold processing, the hardening of the pellet is by intergranular bonding. By utilising hydrothermal reactions of $\text{CaO-H}_2\text{O-SiO}_2$ system

several attempts (mainly by MTU and PTC) have been made¹⁻³ to produce hard pellets and to study their reduction behaviour.

The present investigation deals with the cold bonding of composite pellets of iron ore-Leco-lime and silica utilising the hydrothermal reaction of $\text{CaO-H}_2\text{O-SiO}_2$ system. The advantage of using rice husk ash in the place of natural silica lies in the amorphous nature of silica present in the rice husk ash which is highly reactive towards lime in the pellet mix. The study assumes great importance as it affords a method to exploit the regional raw materials. The Southern part of India suffers from high cost of fuel, which renders the economics of iron production by means of coke very unattractive and uneconomical. It is necessary to use alternate fuels which will eliminate the dependence on coking coals which are even otherwise not abundant in India. Lignite char available at Neyveli, one such source of carbon can be considered for iron production. The paper deals with the studies on the production of cold bonded composite pellets using Bellary-Hospet iron ore and Neyveli Leco char.

EXPERIMENTAL MATERIALS AND METHODS

Materials : The iron ore used in the investigation was obtained from Bellary-Hospet region of Karnataka, India. The sample was crushed and ground to pass through 200 mesh BSS (75 microns). The chemical analysis of the ore is indicated in Table I.

The carbonaceous material (reductant) used in this work was Leco coke from Neyveli Lignite Corporation, India. The Leco lumps were ground to pass through 200 mesh BSS. The assay of this material is shown in Table II. The limestone of size 25 mm was calcined at 1100°C, hydrated and passed through 200 mesh BSS. The calcined lime analysed 90.72% of available lime.

A river sand from Kerala, was used as a source of natural silica. The sand was washed, dried and ground to pass through 200 mesh BSS. This powder analysed 95% SiO_2 . The other form of silica used in this work is from rice husk. The raw rice husk obtained from a rice mill was washed, dried and ignited at 600°C for 15 hours. The white ash thus obtained was very fine passing through 300 mesh BSS. The chemical analysis of this ash is given in Table III.

Methods : The procedure adopted consisted in mixing the iron ore powder with stoichiometric quantity of Leco coke, specified amounts of calcined lime and natural silica flour/rice husk ash in a sand miller with moisture (100 ml/kg of iron ore). Then the mix was taken out and balled in a laboratory disc pelletiser. The pellets thus produced were in a size range of 9-16 mm. These green pellets were allowed to dry at room temperature for about 24 hours. Then the pellets were subjected to steaming in an autoclave at various temperatures/saturated steam pressures. After steaming, the pellets were removed, cooled and the crushing strengths were measured. In each experiment a minimum of 12 pellets were tested and the average crushing strength was recorded.

To study the hydrothermal reaction of $\text{CaO-H}_2\text{O-SiO}_2$ system, a stainless steel bomb was used as per the earlier experimental procedure⁴. The 1:1 mixture of lime and rice husk silica with water was taken in the bomb which was immersed in an oil bath. At specified temperature and time, the bomb was removed from bath, opened and the reaction product was analysed for free lime⁵ present in it.

The product obtained at the end of the reaction was washed well with acetone and then with ether. This was filtered, dried in vacuum and subjected to X-ray diffraction analysis for product identification along with steamed pellets.

RESULTS AND DISCUSSION

Pelletization and strengthening :

Effect of curing time : Initially about a kg each of composite pellets were prepared with stoichiometric amount of carbon and $\text{CaO/SiO}_2 = 1$, using silica flour and husk ash silica separately. These green pellets were kept in open in a tray under ambient conditions to study the effect of curing time on the strength of the green pellets over a period of 240 hours. The results shown in Table IV indicate the advantage with rice husk ash in getting superior strengths. Further, the results indicate that the strength of the pellet does not increase appreciably with increase in curing time beyond 10 days (without steaming) in the case of natural silica, indicative of incomplete reaction between calcium hydroxide and natural/mineral silica and insufficient bonding agent. In the case of rice husk ash the silica is in the amorphous (reactive) form and reacts easily with lime forming more calcium silicate hydrate resulting in better strength of the composite pellets. It is well known that this reaction proceeds faster under hydrothermal conditions. So further pelletisation and strengthening experiments were carried out under hydrothermal conditions.

Effect of temperature/pressure : The effect of temperature/pressure on the strength of the composite pellets at $\frac{8}{3}$ CaO keeping the added $\text{CaO/Silica} = 1$ is shown in Table V. From the results it could be seen that the composite pellet strength continue to increase with an increase in temperature (steam pressure). This indicates that the formation of calcium silicate hydrate (the

chief bonding agent), also increases resulting in improved strength of the pellet. The results also indicate the high reactivity of rice husk ash silica with lime resulting with formation of more calcium silicate hydrate than that with natural silica.

The effect of lime (keeping added $\text{CaO/SiO}_2 = 1$) : The effect of the amount of CaO in the composite pellet on its strength at 200°C is shown in Table VI. These experiments were conducted with additions of CaO and SiO_2 to increase the quantity of bonding material (CSH) available for strengthening the pellets. The results revealed that the strength of the pellet continued to increase with an increase in the addition of CaO in both cases of natural silica flour and rice husk ash silica. But the pellet with rice husk silica always exhibited higher strength compared to pellet with natural silica. This may be attributed to the amorphous silica present in the rice husk ash. However, the increase in CaO and SiO_2 results in lowering the iron content of the pellets with disadvantages of increased slag volume.

The above study revealed that the composite pellets made with rice husk ash and lime are far superior. To understand the strengthening mechanism and the cause for increased strength of the pellets, the investigators felt the need to study in detail the reaction of $\text{CaO-H}_2\text{O-SiO}_2$ (rice husk ash) system under hydrothermal conditions.

Reaction kinetics and strengthening mechanism

Reaction kinetics : The reaction between lime and rice husk silica, under ambient conditions is time consuming whilst under hydrothermal conditions, the reaction is fast and easy to be studied and hence it was adopted in the present study.

The kinetics of this hydrothermal reaction was studied at various temperatures viz. 81.5 to 200°C at C/S ratio = 1. A plot of fraction of lime reacted (α) versus time (t) for the data is shown in Figure 1. From the figure it is clear that from 81.5 to 180°C^{7,8} the reaction exhibits two acceleration periods, but at 200°C the reaction exhibits only one acceleration period. In a polysize sample; it is not essential that all particles will react according to one and the same mechanism. So a consideration of various reaction processes like nucleation and growth

$$[-\ln(1-\alpha)]^{1/3} = k_n \cdot t$$

phase boundary interaction

$$1-(1-\alpha)^{1/3} = k_c \cdot t$$

and diffusion

$$1-2/3 \alpha (1-\alpha)^{2/3} = k_d \cdot t$$

was attempted. All three models mentioned above showed linearity with the experimental data thereby making any one or more of the three processes rate controlling. From the linear plots figure 2,3 & 4 the rate constants corresponding to both acceleration periods for all temperatures were calculated

presented in table VII. The rate constant values show that diffusion process is slower than phase boundary interaction and phase boundary interaction is slower than nucleation and growth. The activation energy values were then calculated from the log k versus $1/T$ plots and was found to be between 8-21 KJ/mole which falls in the range for diffusion controlled reactions.

At 200°C the reaction showed a different trend compared to that of lower temperatures (where the reaction exhibited two acceleration periods). As the temperature increased, the time at which the first acceleration period ended and the second one began became lesser and lesser and at 200°C a distinction between first and second acceleration periods disappeared and the reaction exhibited only one acceleration period. Furthermore, at 200°C a change in the product of the reaction was also observed.

Strengthening mechanism : One of the basic compounds responsible for the strengthening of pellets, briquettes etc. and hardening of cements, mortars etc. has been shown to be calcium silicate hydrate. In the present case, the formation of this gel like compound (CSH-I) has been attributed to be the reason for the increase in strength of the pellet with increase of temperature. From the x-ray diffractogram it was observed that from 81.5 to 180°C, the pure CaO-rice husk ash mixture showed a prominent peak around $d = 3.03 \text{ \AA}$ (fig. 5b) which is characteristic of CSH-I. At 200°C the product of this reaction was observed to be Xonolite. The XRD analysis of the iron ore pellet containing these components showed (fig. 5c) the formation of CSH-I^{11,12} alongwith the other components present in it which remains yet to be understood. In order to confirm the formation of CSH-I, the compound was synthesised by a known method and subjected to XRD. A prominent peak around $d = 3.03 \text{ \AA}$ (fig. 5a) was observed even over here indicating the formation of CSH-I during the steaming process and responsible for strengthening of the pellet.

Reduction studies on composite iron ore - Leco char pellets :

The composite pellets are reported to show better reducibility due to intimate contact of the oxide particles with the reductant and that only very short reduction times are required for metallisation. It has also been reported that the composite pellets could be metallised and melted in 60 minutes in a hot blast cupola. (1-3)

Hence the reduction behaviour of the composite pellets was attempted. Preliminary weight loss experiments (TGA as well as heating of the pellets in crucibles/boats) were carried out on the composite pellets made of Leco char (a) in stoichiometric amount and (b) 10% excess at 20°C per minute heating rate, in nitrogen atmosphere. The results are shown in figure 6. It is evident from the curve that the maximum weight loss occurred from 1000-1150°C evidently due to the reduction of Fe_2O_3 which continued till 1300°C. The chemical analysis of the reduced products obtained in pellets in crucible experiments are indicated in Table VIII which revealed that

metallisation increased with increase of temperature under the experimental conditions. Systematic studies are being taken up on the reduction of composite pellets at various temperatures.

Conclusions : The studies on the production of composite iron ore Leco char pellets by cold bonding technique revealed that the agricultural waste product rice husk ash is capable of strengthening the composite pellets by the formation of calcium silicate hydrate. The pellets have good reducibility.

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TABLE I

Chemical analysis of iron ore

Constituent	%
Fe (Total)	64.60
FeO	0.22
SiO ₂	2.32
Al ₂ O ₃	2.87

TABLE II

Chemical analysis of Leco char

Constituent	%
Moisture	6.15
Volatile matter	17.69
Fixed carbon	70.16
Asn	6.00
Sulphur (Total)	1.76

TABLE III

Chemical analysis of rice husk ash

Constituent	%
SiO ₂	93.91
Fe ₂ O ₃	0.04
Al ₂ O ₃	2.10
CaO	0.40
MgO	0.36
LOI	2.54

TABLE IV

Effect of curing time on the strength of the green pellets

Conditions : Leco char - Stoichiometric
 CaO/SiO₂ - 1
 CaO - 8%

S.No.	Time (hrs.)	Strength of green pellets (kg/p)	
		Natural silica	Rice husk silica
1	24	13	12.5
2	48	16	26.8
3	96	20	45.0
4	120	22	51.5
5	144	23	54.0
6	192	27	57.4
7	240	29	67.5

TABLE V

Effect of temperature/pressure

Conditions : Leco char - Stoichiometric
 CaO/SiO₂ - 1
 CaO - 8%

Sl. No.	Temp. °C	Pressure kg/cm ² approx.	Strength of pellets (kg/p)	
			Natural silica	Rice husk silic
1	80	-	26	68
2	100	1	40	81
3	120	3	45	105
4	140	4	57	126
5	160	6	72	132
6	180	12	115	148
7	200	19	120	179

TABLE VI

Effect of lime on the strength of the pellet

Conditions : Leco char - Stoichiometric
 CaO/SiO₂ - 1
 Temperature - 200°C
 Pressure - 19/cm²

S.No.	CaO %	Strength of the pellet (kg/l)	
		Natural silica	Rice husk silic
1	2	20	28.0
2	3	85	72.0
3	4	47	82.3
4	5	63	110.0
5	6	82	144.0
6	7	90	202.0
7	8	99	258.0
8	9	110	340.0
9	10	125	N.A.
10	12	130	N.A.

TABLE VII

Rate constants for the nucleation, phase boundary interaction and diffusion for the reaction at C/S=1

Sl. No.	Temp. °K	k_{n_1} $\times 10^3$	k_{c_1} $\times 10^4$	k_{d_1} $\times 10^4$	k_{n_2} $\times 10$	k_{c_2} $\times 10^4$	k_{d_2} $\times 10^4$
1	354.5	0.95	3.77	0.79	-	0.97	0.253
2	373.0	1.11	4.60	0.98	-	1.09	0.326
3	383.0	1.15	6.03	1.27	-	1.38	0.417
4	412.0	1.27	7.59	1.80	-	1.74	0.634
5	433.0	1.47	8.75	2.37	-	-	-
6	453.0	1.63	12.70	2.78	-	3.57	1.540
7	473.0	0.73	6.07	2.87	-	-	-

TABLE VIII

Chemical analysis of reduced pellets

Raw Pellets : Stoichiometric carbon : Total Fe = 43.37% & Fe²⁺ = 0.36%
 10% excess : Total Fe = 41.16% & Fe²⁺ = 0.32%

S.No.	Temp. °C	Stoichiometric				10% Excess			
		Total Fe %	Fe ²⁺ %	Fe ⁰ %	Metallization %	Total Fe %	Fe ²⁺ %	Fe ⁰ %	Metallization %
1	1000	52.96	17.04	2.40	4.37	50.16	17.45	3.53	7.04
2	10745	59.98	45.59	14.46	22.96	56.99	43.96	16.06	28.18
3	1150	70.94	59.72	45.63	63.05	68.94	59.13	49.13	71.27
4	1225	72.54	62.79	48.00	66.16	71.34	65.16	53.34	74.80
5	1275	75.90	64.71	54.13	71.40	71.64	69.78	55.00	76.76

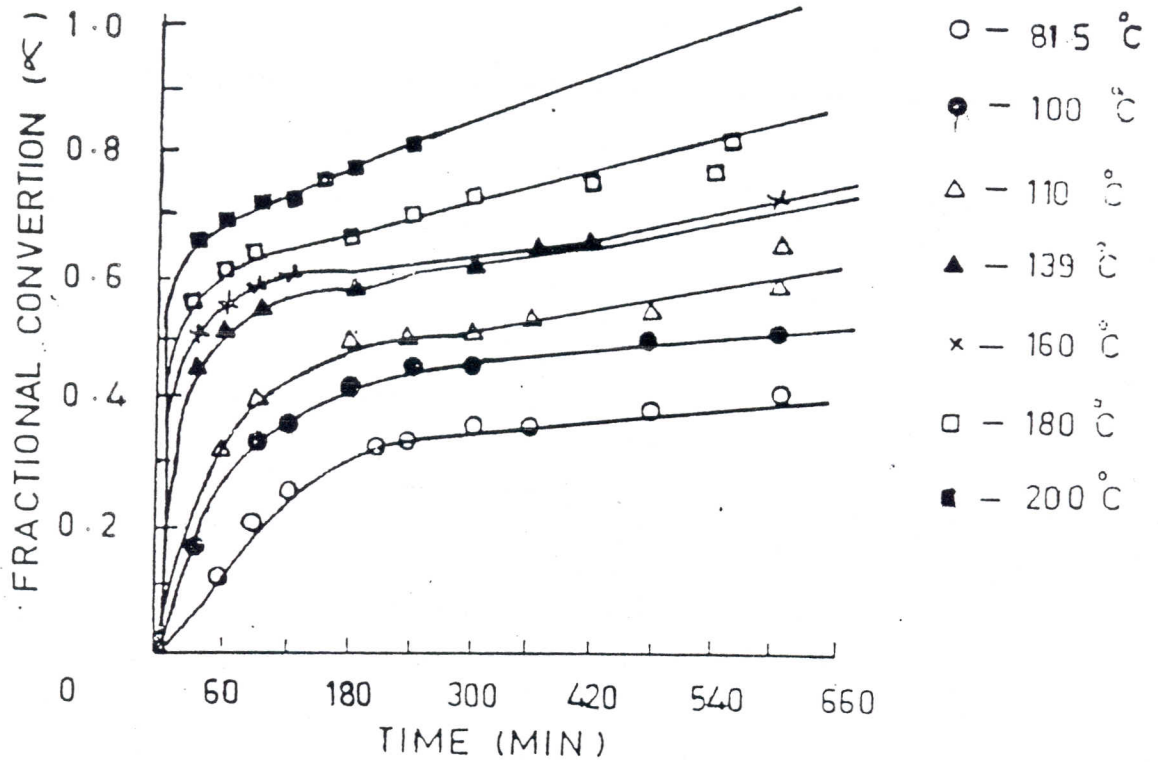


Fig.1 Effect of temperature on lime, RHA reaction at C/S = 1

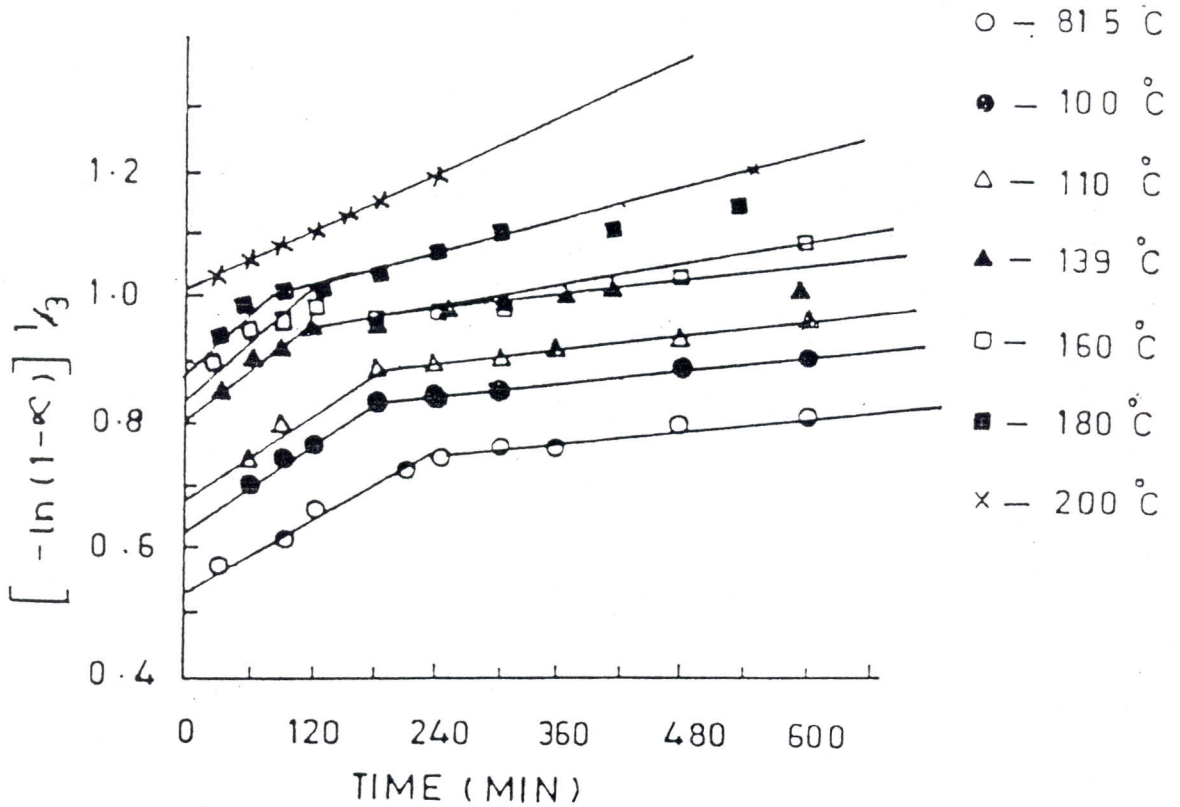


Fig.2 $[-\ln(1-\alpha)]^{1/3}$ vs time plots at C/S = 1.

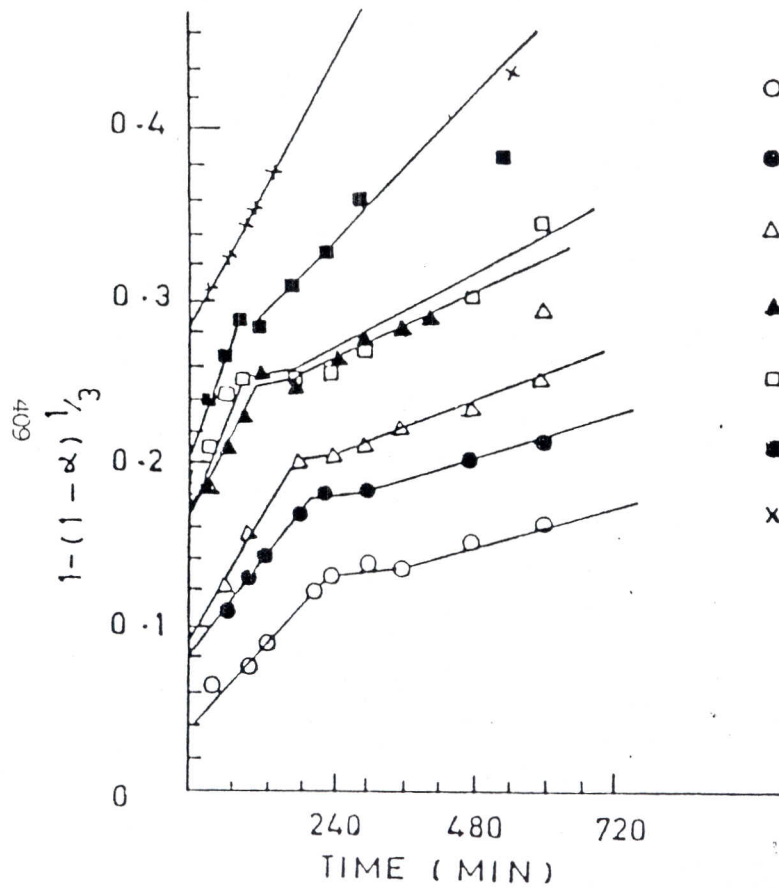


Fig. 3 $1 - (1 - \alpha)^{1/3}$ vs time plots at C/S = 1.

- - 81.5 °C
- - 100 °C
- △ - 110 °C
- ▲ - 139 °C
- - 160 °C
- - 180 °C
- x - 200 °C

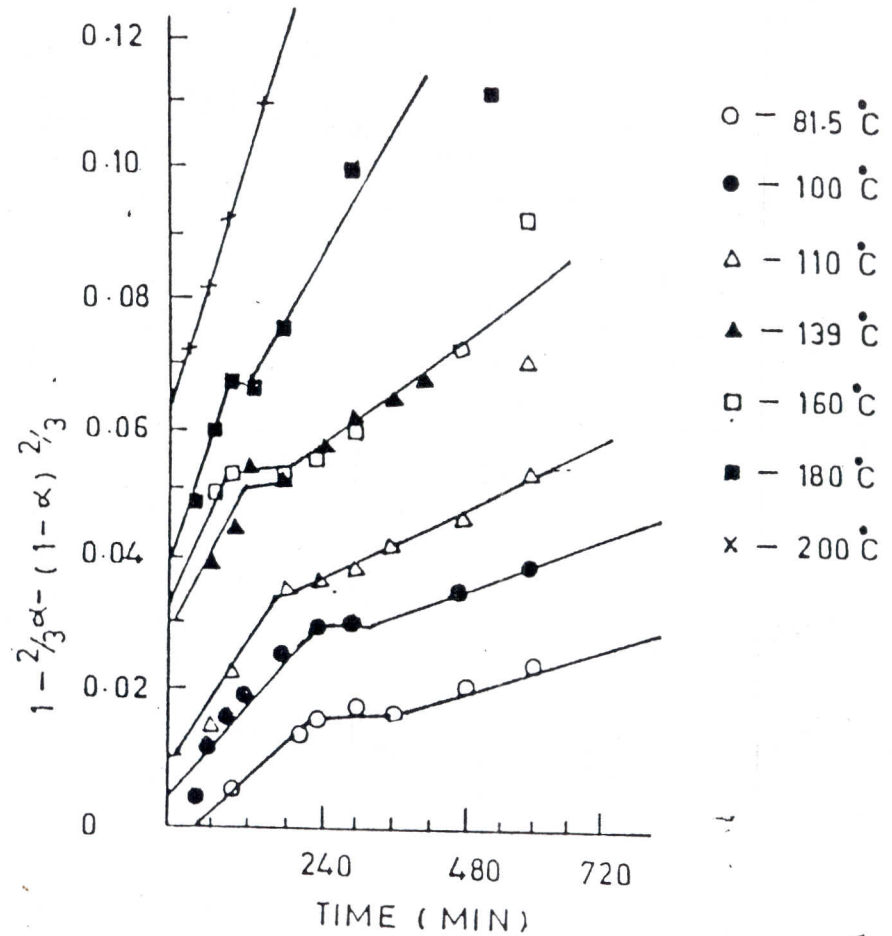


Fig. 4 $1 - \frac{2}{3} \alpha (1 - \alpha)^{2/3}$ vs time plots at C/S = 1.



Fig.5 XRD of (a) synthetic CSH-I (b) Reaction product at 180°C and (c) steamed composite pellet

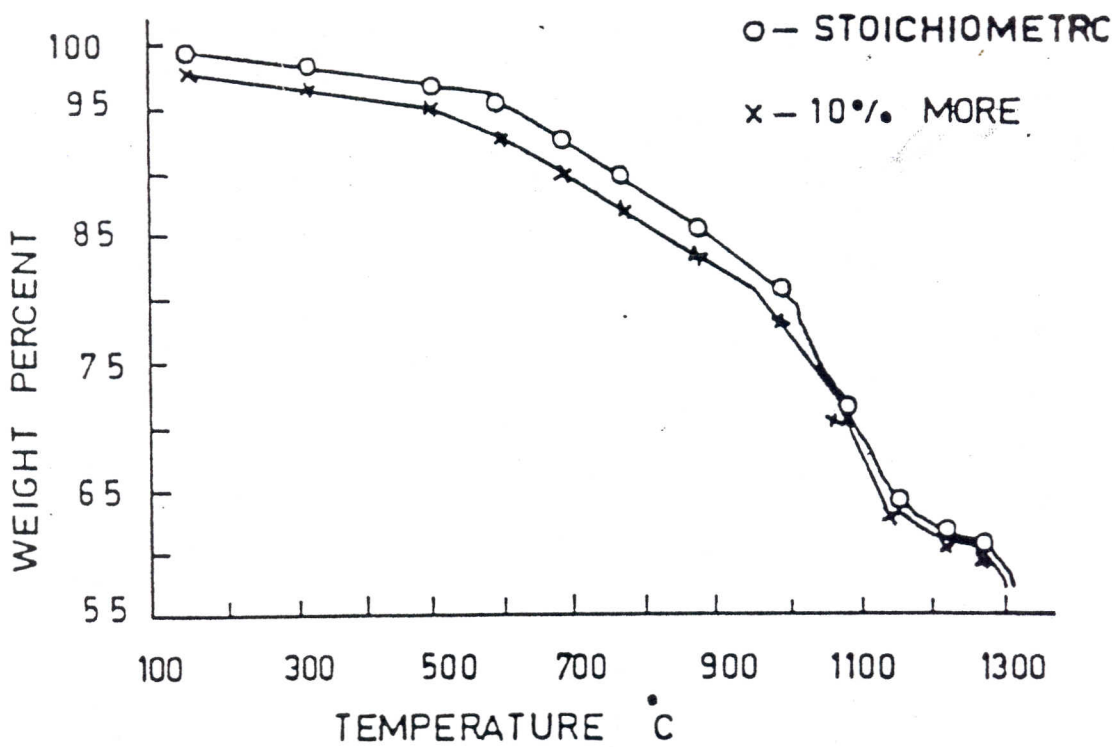


Fig.6 Weight loss of composite pellets vs temperature.