

STUDIES ON THE PRODUCTION OF PLASTER OF PARIS FROM DISCARDED MOULDS

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Abstract : Investigations have been made to develop a simple method to convert discarded moulds in ceramic industry to Plaster of Paris. With this in view, physical and chemical properties of used moulds, Plaster of Paris, gypsum and the products obtained by firing used moulds under different conditions have been determined. Monoclinic form of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ has been identified in the used moulds while Plaster of Paris contains β form of $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$. DTA and XRD analysis show that a temperature lower than 350°C but higher than 170°C is required for the conversion. Rapid heating rates are required for the formation of $\beta - \text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ which gives soluble anhydrite at 170°C . At temperatures higher than 350°C , soluble anhydrite is transformed into an inactive form. Good quality Plaster of Paris could be produced by heating powdered moulds at 180°C for 2 hours in an open atmosphere. Breaking strength, chemical composition and other properties of the product thus obtained conform to the standard requirements of commercial Plaster of Paris.

1. Introduction

Plaster of Paris is produced by calcining gypsum. The main deposits of gypsum are found in United States, France, West Germany, Poland and Austria. A large quantity of the world production of Plaster of Paris is used in the ceramic industry for the manufacture of moulds and as a cementitious material for construction purposes.² It is also used for the manufacture of wall boards and for dental and orthopaedic work.²

In Sri Lanka, plaster of Paris is mainly used for making tableware and sanitaryware moulds in the ceramic industry and as a binding material for plastering purposes. In 1986, the total production of moulds at the Ceylon Ceramics Corporation, Piliyandala, was around 32-35 metric tons per month. After using the moulds for a certain period, these are mainly discarded as a waste material. Some of these have been used for the manufacture of writing chalk and for land filling. Plaster of Paris is imported to

Sri Lanka at a very high cost and therefore, it is important to study the possibility of recycling the Plaster of Paris. In order to develop a method of recycling, it is essential to study the physical and chemical properties of used moulds and Plaster of Paris.

In the present study, investigations have been made in the laboratory scale, to determine the most suitable conditions of regenerating Plaster of Paris from used moulds.

2. Experimental

Used moulds were ground to pass the sieve (300 μm , mesh No.50) and burnt under two different conditions, (i) in a muffle furnace and (ii) in a special vessel (Figure 1) using burners. The constituents in used moulds, Plaster of Paris and the fired products were determined by powder X-ray diffraction with $\text{Cu K}\alpha$ radiation. Thermal analyses (DTA, TG and DTG) of used moulds, gypsum, Plaster of Paris and the fired products were done using a Thermal Analyzer model NETZSCH STA 409. Transverse breaking strengths have been determined by a standard procedure.⁵

Chemical analyses of used moulds and the fired product for CaO , Al_2O_3 , SO_3 were done using gravimetric methods.¹ Fe_2O_3 was determined by a titrimetric method.¹ Na_2O and K_2O were estimated by using a Flame Photometer and MgO was determined by using an atomic absorption spectrometer. SiO_2 was determined by the HF treatment.³

3. Results and Discussion

3.1 Physical Properties of used moulds and Plaster of Paris

3.1.1 X-ray Diffraction Analysis

Powder X-ray diffraction patterns of crockery and sanitaryware moulds showed the presence of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in the monoclinic form. Other compounds were not found in detectable quantities. Imported Plaster of Paris showed the presence of hexagonal type of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$. XRD patterns of used moulds and Plaster of Paris are given in Figure 2.

3.1.2 Thermal Analysis

Thermal analyses of used moulds, gypsum and Plaster of Paris were carried out under different conditions and the DTA curves are given in Figure 3. DTA curve of gypsum showed two significant endothermic peaks. The large

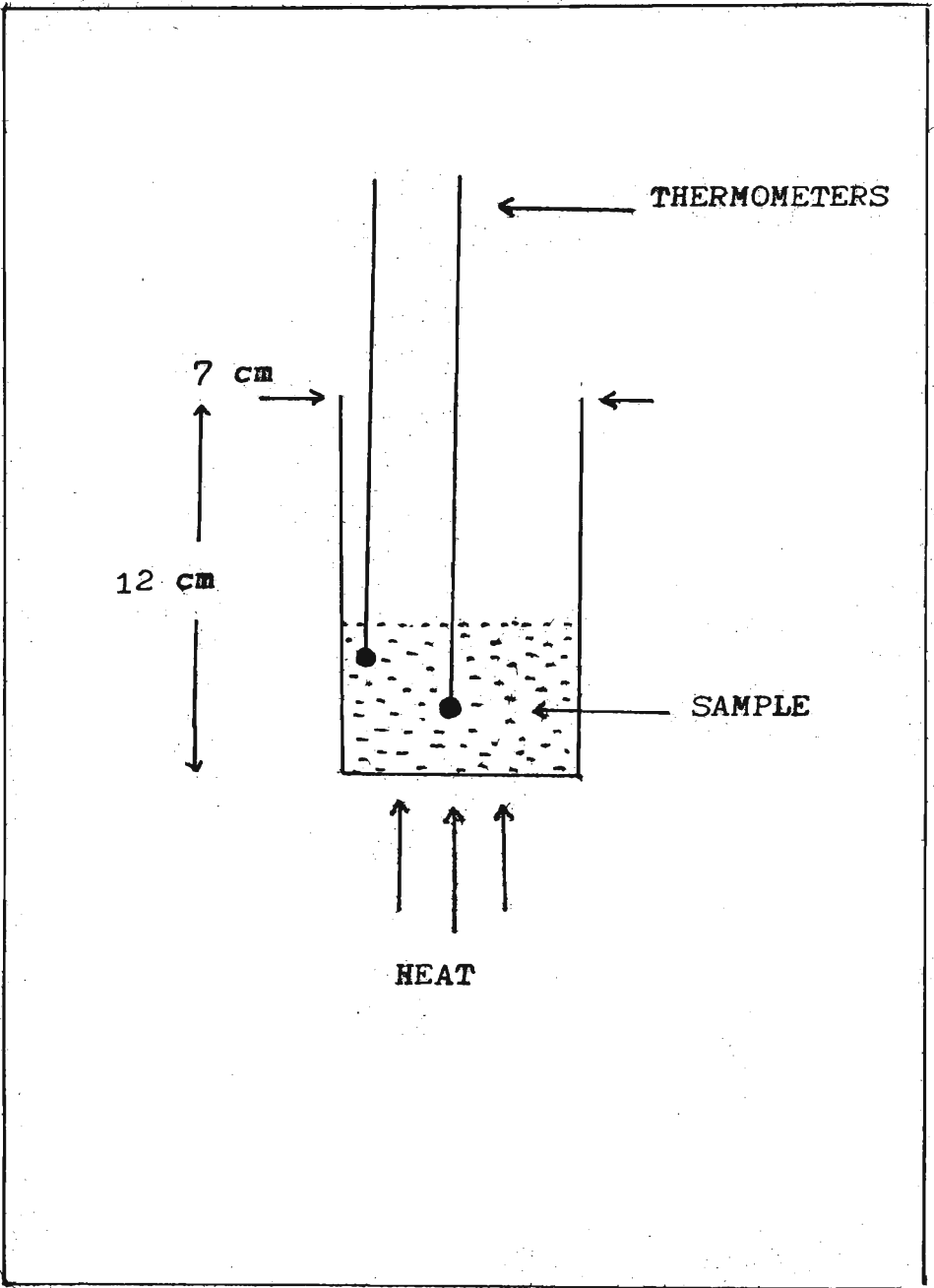


Figure 1. Vessel used for burning used moulds

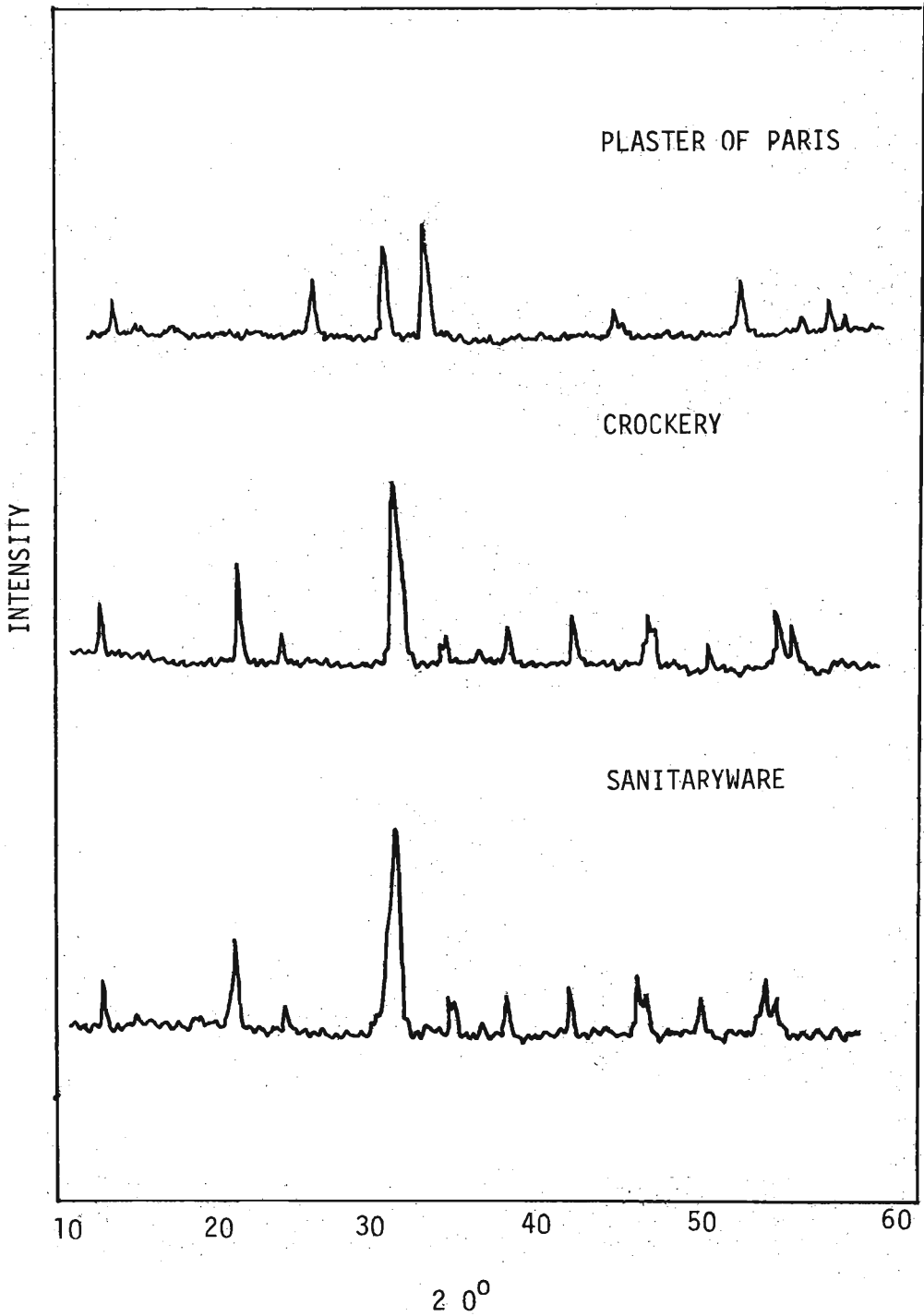


Figure 2. XRD patterns of used mould and Plaster of Paris

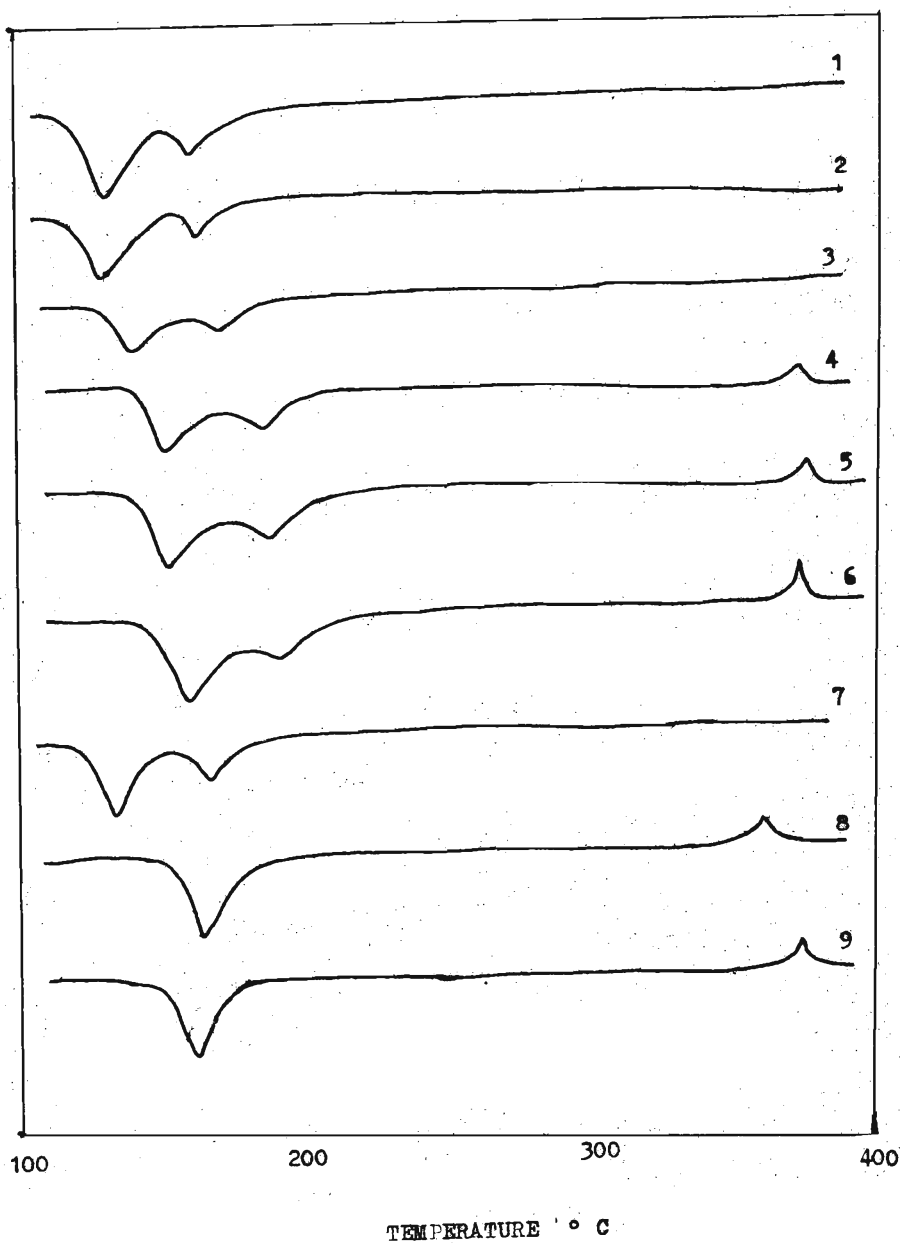


Figure 3. DTA curves of used mould, gypsum, Plaster of Paris and the fired product.

N.B. 1,3,4,5 and 6 are thermograms of used mould at heating rates 2° , 5° , 10° , 15° and 20° C per minute respectively. No.2 is a thermogram taken at 2° C per minute of a sample of used mould which has been preheated at 45° C for 4 hrs. 7,8 and 9 are thermograms for gypsum, Plaster of Paris and the fired product at the heating rate of 2° C per minute, respectively.

endotherm at lower temperature (130°C) is due to the loss of 1.5 molecules of H₂O from CaSO₄.2H₂O. The reaction for the conversion is as follows.



The small endotherm at higher temperature (170°C) indicates the loss of 0.5 molecules of H₂O from CaSO₄.0.5H₂O. The reaction for the conversion is as follows.



A very small endothermic peak was observed at 730°C. This is probably due to the decomposition of magnesite which is present as an impurity.

The DTA curves of used mould (1,2,3,4,5 and 6) were similar to gypsum, but slight variations of the peak positions were observed. These results show that the CaSO₄.2H₂O form of the used plaster undergoes dehydration through the formation of CaSO₄.0.5H₂O. In addition to these two major endotherms, samples 4,5 and 6 which were analyzed at higher heating rates (10°, 15° and 20° C/min.) showed a small exothermic peak at 350–380°C and this is due to the phase transformation of soluble anhydrite (CaSO₄) to an insoluble form. It has been found that this kind of transformation is only possible for β form of CaSO₄.0.5H₂O.⁴ There are two types of hemihydrates, α and β. The α form is more stable² and does not undergo this type of transformation. These results indicate that the anhydrite is formed through the formation of β –CaSO₄.0.5H₂O at higher heating rates whereas at low heating rates (2 and 5°C/minute) the anhydrite is produced through the formation of α–CaSO₄.0.5H₂O. The exotherm at 350–380°C was found to be more sharp and the intensity increases with increase of heating rate. The insoluble form of CaSO₄ is an inactive form and does not undergo rehydration as the normal active CaSO₄. Therefore temperature should not be allowed to exceed 350°C, since the active form of anhydrite is transformed into an inactive form at this temperature.

DTA curve of commercially available Plaster of Paris showed an endotherm at 170°C and a small exotherm at 350°C. These are due to the loss of 0.5 molecules of H₂O from CaSO₄.0.5H₂O and the phase transformation of soluble anhydrite to an insoluble form. This result indicates that the commercial type of Plaster of Paris constitutes β –CaSO₄.0.5H₂O.

TG curve of the used moulds showed one large and one small weight loss and these are due to the loss of 1.5 and 0.5 molecules of H₂O respectively. DTG curve also showed two sharp peaks due to these two weight losses. Figure 4 shows TG, DTG and DTA curves of the used moulds.

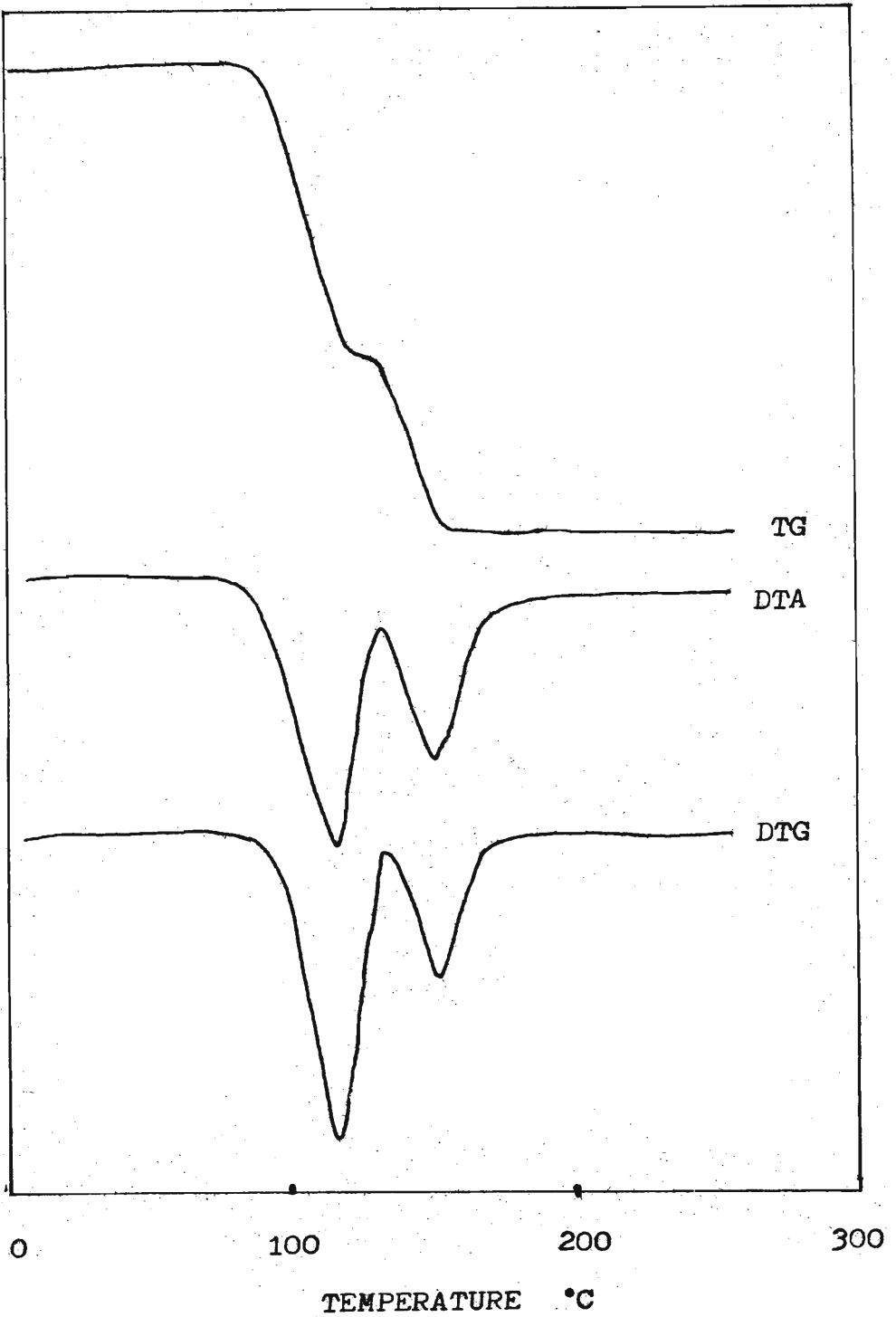


Figure 4. TG, DTG and DTA curves of used moulds

Table 1 shows the positions of the two endotherms and percentage weight losses of the used moulds. It was found that the position of the endotherms depend on the heating rate of the sample. The peak temperatures of each reaction increases with the increase of heating rate and the separation between the two endothermic peaks was clearly observed when the heating rate was 2°C/minute.

Table 1. Peak Position and Percentage Weight Loss of the used Mould

	Heating Rate °C/minute			
	2	2*	5	10
Large endotherm (°C)	130	130	140	150
Small endotherm (°C)	160	160	175	180
Large weight loss (% by weight)	14.1	14.1	14.3	—
Small weight loss (% by weight)	4.5	4.5	4.2	—

Note: *This sample has been preheated at 45°C for a period of 4 hrs.

The percentage weight losses are almost the same in all the samples and the ratio of these two losses in each sample is roughly three. This is because the weight losses are associated with the loss of 1.5 and 0.5 molecules of H₂O respectively. One sample analyzed at 2°C/minute was kept in an oven at 45°C for 4 hrs. before the analysis. The results showed that there is no appreciable effect of preheating of the sample at this temperature on percentage weight loss.

3.2 Chemical Analysis of used Plaster of Paris Moulds and the Product

Table 2 shows the chemical composition of used moulds and the product obtained by burning at 180°C for 2 hrs. Major impurities such as SiO₂, Fe₂O₃, Al₂O₃ and MgO were found in appreciable quantities. Na₂O and K₂O were also found in detectable quantities. It has been observed that the contents of bound H₂O, CaO, MgO and SO₃ show significant differences in the two samples. The low amount of bound H₂O in the product is due to the dehydration of 1½ molecules of H₂O. The contents of CaO and SO₃ in the product are high when compared to that of the used mould. This is due to the loss of 1½ molecules of H₂O during calcination process. Slightly higher quantity of the MgO in the product indicates the dehydration of hydrated MgO during thermal treatment.

Table 2. Chemical Composition of Used Moulds and the Product

Constituent % by weight	Used Mould	Product
Free H ₂ O	0.15	0.16
Bound H ₂ O	20.05	5.89
SiO ₂	1.80	1.82
Fe ₂ O ₃	1.46	1.49
Al ₂ O ₃	0.34	0.41
CaO	31.20	36.74
MgO	0.21	0.27
Na ₂ O	0.05	0.05
K ₂ O	0.11	0.14
SO ₃	44.55	52.43

The amount of CaSO₄·2H₂O in the moulds and the amount of CaSO₄·½H₂O in the product are 95.8% and 95.1% respectively. The contents of CaSO₄·2H₂O in moulds and CaSO₄·½H₂O in the product conform to the requirements of gypsum and Plaster of Paris specified in ASTM.

3.3 Heat Treatment of used Plaster

3.3.1 Burning in a muffle furnace

The samples obtained by burning at 140°C and 180°C contain the hexagonal type of CaSO₄·0.5H₂O. Then the dehydration occurs with increase of temperature and the samples obtained at 300°C and 550°C show the presence of CaSO₄. The XRD patterns were taken at room temperature although anhydrite is formed at 180°C, on cooling in air it transforms into hemihydrate. As such the XRD powder patterns of samples heated at 140°C and 180°C are similar showing the presence of hemihydrate in both cases. The XRD patterns of the fired products are shown in Figure 5 and their *d* values and the relative intensities are given in Table 3.

3.3.2 Burning in a special vessel using burners

Used mould samples were burnt at 140 ± 3°C, 180 ± 3°C, 300 ± 3°C and 550 ± 3°C for 2 hrs in a special vessel (Figure 1) and transverse breaking strength of the products were determined. Results indicate that the strength of the original Plaster of Paris is the highest and the strength of the sample

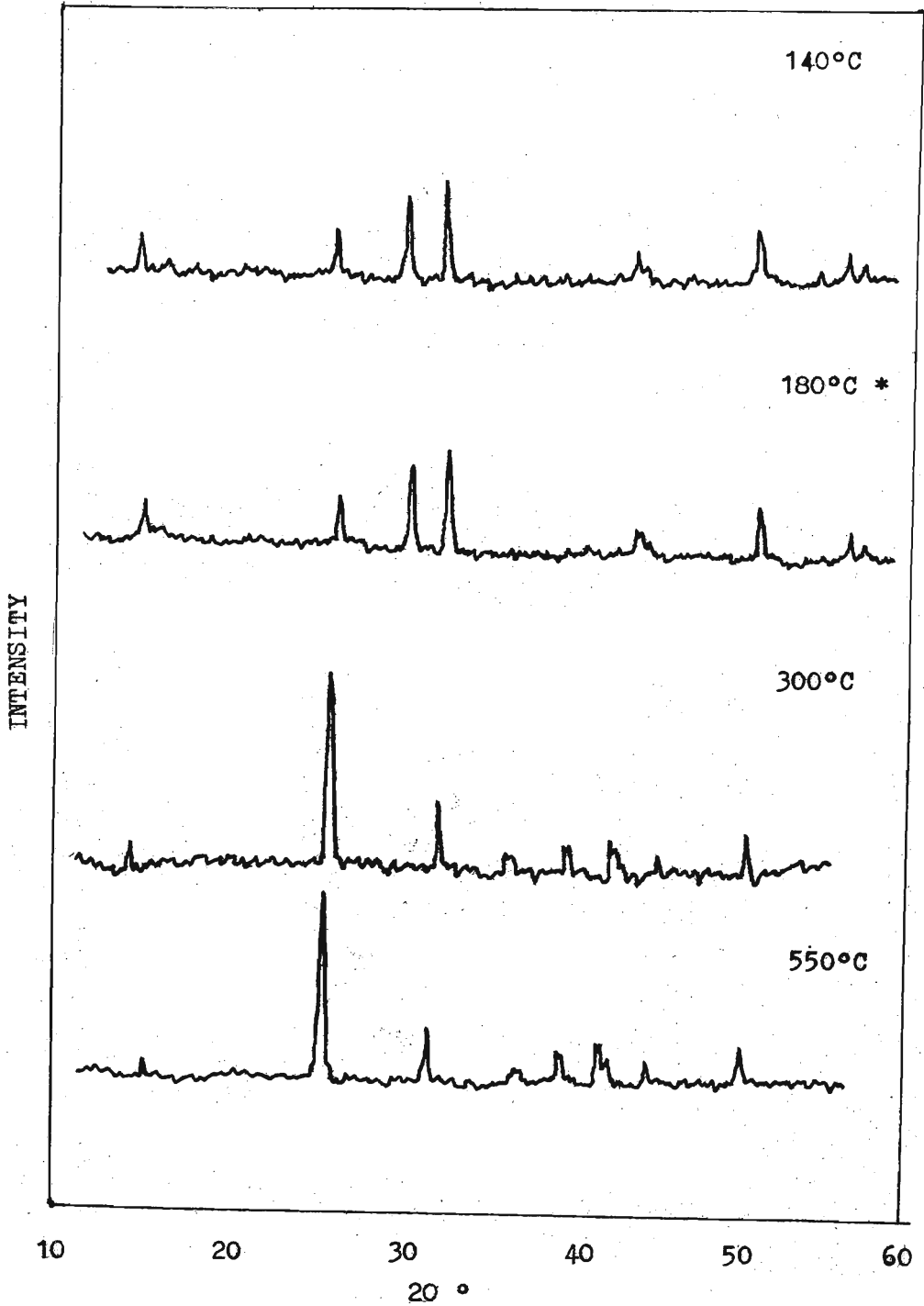


Figure 5. XRD patterns of products obtained by burning used moulds

N.B. * gives the most suitable burning condition

Table 3. X-ray Diffraction Data of Fired Samples

140°C/2 hrs.		180°C/2 hrs.		300°C/2 hrs.		550°C/2 hrs.	
d(A°)	I	d(A°)	I	d(A°)	I	d(A°)	I
6.10	57	6.15	57	6.71	17	6.70	17
3.51	60	3.52	60	6.55	15	6.55	15
3.04	90	3.04	92	3.48	100	3.48	100
2.85	100	2.85	100	2.83	33	2.83	33
2.12	32	2.15	32	2.43	11	2.45	12
1.86	60	1.86	60	2.32	20	2.32	20
1.72	32	1.70	33	2.18	23	2.19	24
1.65	22	1.67	22	2.17	17	2.17	17
				2.05	15	2.07	13
				1.86	20	1.86	21
				1.74	17	1.74	17

obtained at 180°C is very close to that of Plaster of Paris. Therefore this result shows that the most suitable temperature of burning used plaster to obtain Plaster of Paris is 180°C. The strength increases upto 180°C and decreases with increase of temperature. It is significant that there is a sudden drop of strength when temperature rises from 300°C to 550°C. This is because the active form of CaSO_4 converts to an inactive form during this temperature range as shown in DTA. Table 4 shows the breaking strength of the products.

Table 4. Breaking Strength of the Products and Plaster of Paris

Sample	Temperature (°C)	Duration (hrs.)	Breaking strength (grams)
Calcined product	140	2	267
Calcined product	180	2	375
Calcined product	300	2	322
Calcined product	550	2	117
Plaster of Paris			392

Used mould samples were also burnt at $180 \pm 3^\circ\text{C}$ for 1,2,3 and 4 hrs and breaking strength of the products were determined. It was found that the breaking strength of the product increases with increase of duration of burning upto 2 hrs. and remains constant. It has been observed that there is no appreciable effect of further burning beyond 2 hrs, on the quality of the product. These results indicate that the most suitable duration of burning of used moulds is 2 hrs. Breaking strength of the products are given in Table 5.

Table 5. Breaking Strength of the Products obtained by Burning Used Mould at 180°C for Different Durations

Duration of Burning (hrs.)	Breaking Strength (grams)
1	280
2	375
3	375
4	370

3.4 Properties of the Fired Product

Powder XRD pattern of the product obtained by burning used moulds at 180°C for 2 hours in an open atmosphere is almost similar to that of Plaster of Paris. DTA of the product shows an endotherm at 170°C and an exotherm at 380°C . These two peaks in DTA are due to the loss of $\frac{1}{2}\text{H}_2\text{O}$ from $\beta\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ to form anhydrous CaSO_4 and the transformation of soluble anhydrite to the insoluble form respectively. Relevant DTA curves are shown in Figure 3 while the XRD pattern of the product is given in Figure 5.

It is apparent that the material produced by calcination of the used moulds at 180°C consists mostly of the hemihydrate. The calcination temperature 180°C is however higher than the dehydration temperature of hemihydrate. Therefore the product of calcination at 180°C is probably the soluble anhydrite, which on cooling and exposure to air forms the hemihydrate.

Breaking strengths of the products obtained by burning the used moulds at different temperatures are compared with the breaking strengths of Plaster of Paris in Table 4. The transverse breaking strength of the product obtained at 180°C (375g) is very similar to that of Plaster of Paris (392 g). The products obtained at other temperatures have much lower breaking strengths. Thus, it is clear that the optimum temperature of conversion is about 180°C .

4. Conclusions

Plaster of Paris can be produced by the heat treatment of discarded moulds under different conditions and the quality of the product thus obtained depends on the temperature and duration of burning. No appreciable differences have been observed in the products obtained by the two methods of burning used in the present study. Burning in a kiln requires high expenditure and as such open burning method seems to be more economical for a commercial process. DTA studies have shown that a temperature higher than 140°C and a rapid heating rate are required for the formations of $\beta\text{-CaSO}_4\cdot 0.5\text{H}_2\text{O}$ which undergoes further dehydration at 170°C to give an active form of anhydrite. Since the active form of CaSO_4 is transformed into inactive form at about 350°C , the burning temperature should be controlled below 350°C .

A temperature of 180°C and a heating duration of 2 hours are found to be most suitable for the conversion of used moulds to Plaster of Paris. Physical and chemical properties of the product thus obtained are very similar to those of commercial Plaster of Paris. Therefore, the product obtained under these conditions can be used for the manufacture of new moulds and as a cementitious material for construction purposes.

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References

1. ANNUAL BOOK OF ASTM STANDARDS (1980) Part 13: Cement, Lime, Gypsum, American Society for testing and materials.
2. APPELYARD, F.C. (1975) Gypsum and Anhydrite, *Industrial Minerals and Rocks*, American Institute of Mining, Metallurgical and Petroleum Engineers, Inc., New York.
3. BENNETT, H. HAWLEY, W.G. (1965) *Methods of silicate analysis*, 2nd edition, Academic Press, London.
4. MACKENZIE, R.C. (1972) *Differential thermal analysis*, Part 2. Academic Press, London.
5. Specification for School chalk (1971). Sri Lanka Standard Institution, Ceylon Standard C.S. 114.