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THERMOCHEMICAL ALTERATIONS ON HEATING HARDENED HIGH-LIME MAGNESIOCHROME REFRACTORY CEMENTS

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ABSTRACT

The thermochemical changes occurring on heating hardened high-lime magnesiochrome refractory cements were studied using differential thermal and thermogravimetric analysis techniques. There were two stages of weight loss. The first ended at 400°C, including the decomposition of Mg-oxychloride as well as dehydration of Ca-chromate dihydrate and brucite. The second loss in weight began at 550°C and came to an end at 900°C, corresponding to the dehydration of portlandite as well as decarbonization of secondary Mg- and Ca-carbonates. There was a weight gain between 400 and 550°C due to the combination of Ca-monochromite with lime and oxygen to form Ca-chromate. DTA showed an exothermic peak corresponding to this reaction at 430°C. The data obtained revealed an endothermic reaction at 1030°C, corresponding to the dissociation of Ca-chromate.

INTRODUCTION

The ternary system $MgO-CaO-Cr_2O_3$ is known to be of remarkable importance in refractory technology. It is particularly important when stabilization of dolomitic materials with chrome ore has to be dealt with. The refractory properties and identification of mineral species in this system were the subject of most of the previous works.

According to Ford and Rees [1], firing of high-lime batches belonging to the $MgO-CaO-Cr_2O_3$ system in an oxidizing atmosphere leads to the formation of Ca-chromate chromite ($9\ Cao \cdot 4\ CrO_3 \cdot Cr_2O_3$), which was found to convert, at its melting point (1228°C), into CaO and Ca-monochromite, both of which are highly refractory [2–4].

The possibility of using magnesiochrome compositions of high-lime content as refractory cements has been discussed previously [5]. This was followed by a study of the relation between compositional variations in clinkers and technological properties of cements prepared therefrom [6].

It is well known that any changes occurring in a given refractory cement when exposed to heat influence to a large extent the whole unfired mass in which it is incorporated. Therefore, the study of the effect of heat on a given refractory cement has always proved essential. It has to be mentioned here that the effect of heat is actually induced by thermal alterations, influencing the hydration products in the hardened cement.

The aim of the present work is to determine the thermochemical changes occurring on heating hardened magnesiochrome refractory cements of high-lime content. This was carried out using differential thermal and thermogravimetric analysis techniques.

EXPERIMENTAL

In the present study five cements were investigated, consisting of periclase and Ca-chromate chromite in different proportions (Table 1). The cement powders (0.086–0.00 mm) were mixed with 8% by weight of 30% $MgCl_2 \cdot 6H_2O$ solution to enhance hydration [7,8]. For comparison, another series of samples was prepared with 8% by weight distilled water. Cylindrical samples (1.60 cm diameter and 1.50 cm height) were shaped by pressing in a steel mould at 800 kg cm^{-2} specific pressure. Air-curing was carried out at 75% relative humidity, and 25 ± 1°C. After air-curing for 28 days, samples were dried at 110 ± 5°C for 24 h. The hardened cement samples were kept in a desiccator on a soda lime–$CaCl_2$ mixture to minimize atmospheric carbonization. The cement samples were crushed and ground directly before analysis in an agate mortar before passing through a 100 mesh B.S. sieve.

Differential thermal analysis (DTA)

An automatic apparatus of the type Linseis SELB BAY was applied in the present study. During the analysis, the rate of heating was 10°C $min.^{-1}$.

TABLE 1

Phase composition of cement powders

Cement No.	Periclase (wt.%)	Ca-chromate chromite (wt.%)
1	83.5	16.5
2	70.0	29.9
3	65.7	34.3
4	65.2	34.8
5	62.9	37.1

Thermogravimetric analysis (TGA)

A laboratory installed TGA apparatus was used in the present study (Fig. 1). Rate of heating was kept at 10°C min^{-1}.

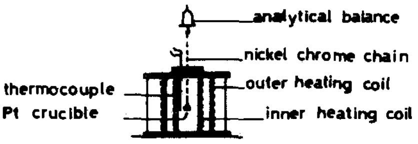

Fig. 1. Schematic diagram of the thermogravimetric analysis apparatus.

RESULTS AND DISCUSSION

Differential thermal analysis (DTA)

Differential thermal analysis is well known as a very useful tool in phase constitution determinations; nevertheless, it cannot be used alone for this purpose [9]. Therefore, the phase constitution of the hardened refractory magnesiochrome cements was determined using DTA, in addition to X-ray and optical microscopy [10]. The studied cements were found to consist of brucite, portlandite, Ca-chromate dihydrate and Ca-monochromite. Due to atmospheric carbonization of brucite and portlandite, μ-$CaCO_3$, $CaMg(CO_3)_2$ and $Mg_3Ca(CO_3)_4$ were formed. As the studied cements were shaped by semi-dry pressing, periclase and Ca-chromate chromite existed as unhydrated cores.

Samples prepared with water

The DTA curves of these samples are shown in Fig. 2. These curves reveal the occurrence of an endothermic effect at 200°C. which corresponds to the dehydration of Ca-chromate dihydrate [11]. The intensity of this effect increased with the increase of Ca-chromate chromite content, i.e., from cement 1 to cement 5. In the case of cement 1, a small endothermic effect took place at 280°C which may correspond to a second step in the dehydration of Ca-chromate dihydrate. The appearance of this peak in the case of cement 1 only may be due to dilution effect induced by the higher content of periclase and its derivatives [12]. The endothermic effect at 350°C corresponds to the dehydration of brucite [13,14]. The intensity of this effect decreased with the decrease of periclase content, i.e., from cement 1 to

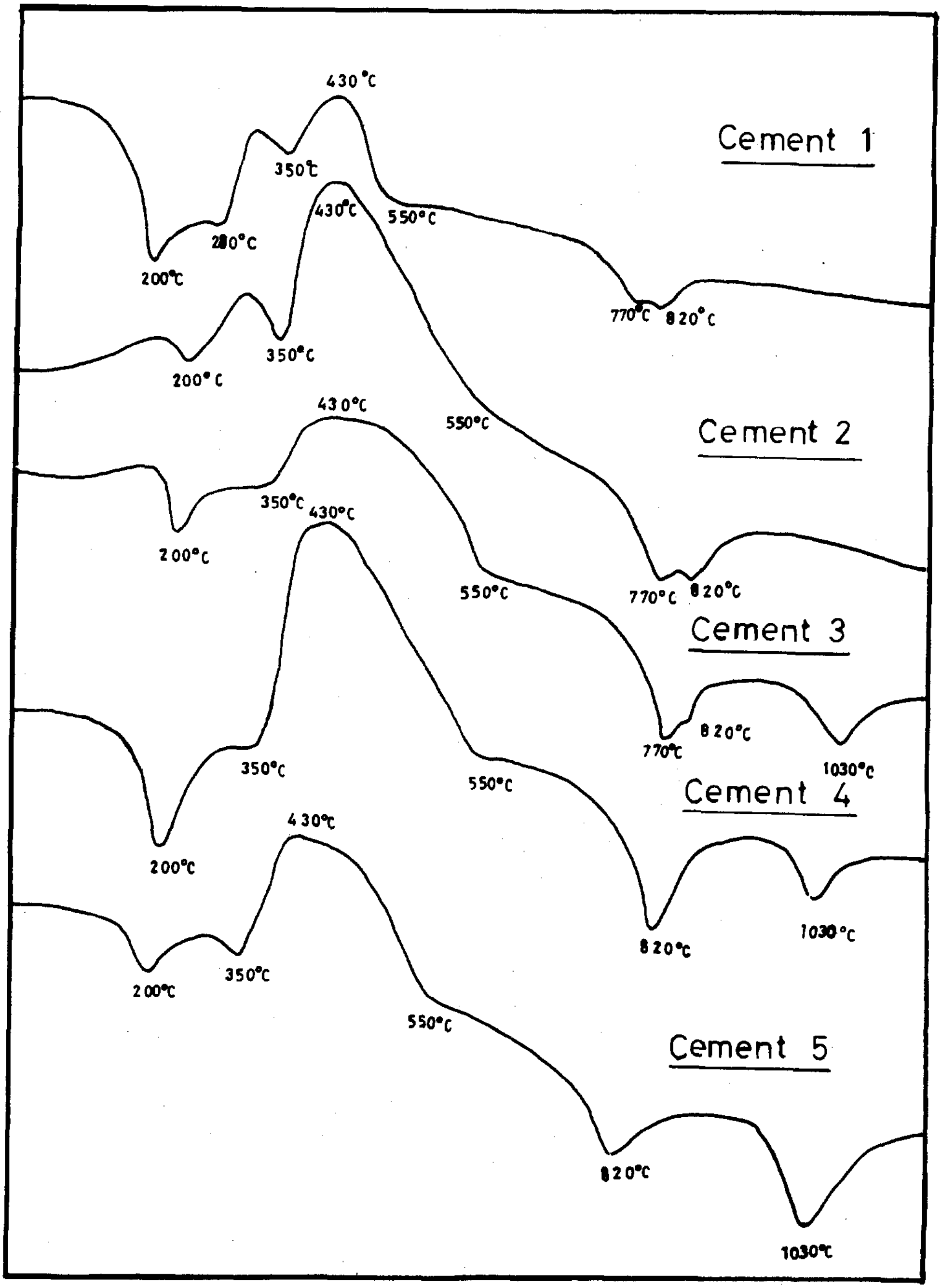

Fig. 2. DTA curves of the hardened magnesiochrome cements (mixed with distilled water).

cement 5. The exothermic effect taking place at 430°C may correspond to the reaction of Ca-monochromite with lime and oxygen, and formation of Ca-chromate. This oxidation reaction was reported by Ford and Rees [15] to take place at 500°C. The relatively lower temperature recorded in the present study may indicate a higher reactivity in the Ca-monochromite liberated from the hydration of Ca-chromate chromite. The broad endothermic effect at 550°C corresponds to the dehydration of portlandite [11]. The first three cements showed a composite endotherm of two peaks at 770 and 820°C. These peaks correspond to the decarbonization of secondary Mg- and Ca-carbonates, respectively [13,14]. The peaks in the case of cement 3 resemble those characterizing the decarbonization of dolomite. In the case of cements 4 and 5, the individual peak corresponding to the decomposition of Mg-carbonate became undetectable. This may indicate a remarkable decrease in the amount of this constituent. The DTA curves of cements 3, 4 and 5 revealed the occurrence of an endothermic effect at 1030°C, which may correspond to the dissociation of Ca-chromate, with loss of oxygen and formation of the true binary compound Ca-monochromite and liquid [15]. This was ascertained by the disappearance of the bright yellow chromate colour, and limited consolidation in the samples at the end of the DTA run.

Samples prepared with magnesium chloride

The DTA curves of samples prepared with 30% $MgCl_2 \cdot 6\ H_2O$ solution are shown in Fig. 3. These curves show an endothermic effect at 220°C, following directly the Ca-chromate dihydrate effect. The peak corresponds to the decomposition of magnesium oxychloride [16–18]. The intensity of this endotherm decreased with the decrease in periclase content, i.e., from cement 1 to cement 5. On the other hand, the 350 and 550°C endotherms did not show remarkable variation. For the same reason, as in case of samples prepared with distilled water, the 280°C endotherm could be detected only in cement 1. The small endotherm at 670°C corresponds to the decarbonization of secondary Mg-carbonate [13,14]. These peaks have not been detected in samples prepared with distilled water, which may indicate enhancement of hydration when mixing was carried out with $MgCl_2 \cdot 6\ H_2O$ solution. Additional evidence for the hydration enhancement in these samples is the appearance of the 770 and 820°C composite effect in the DTA curves of the five cements. The resemblance between this effect and that characterizing dolomite decomposition is noticeable here. This composite effect had a reversed character in the case of cement 5, which may indicate a larger content of the Ca-carbonate constituent. In this series of samples, the Ca-chromate dissociation endotherm at 1030°C showed a noticeable intensity increase from cement 3 to cement 5.

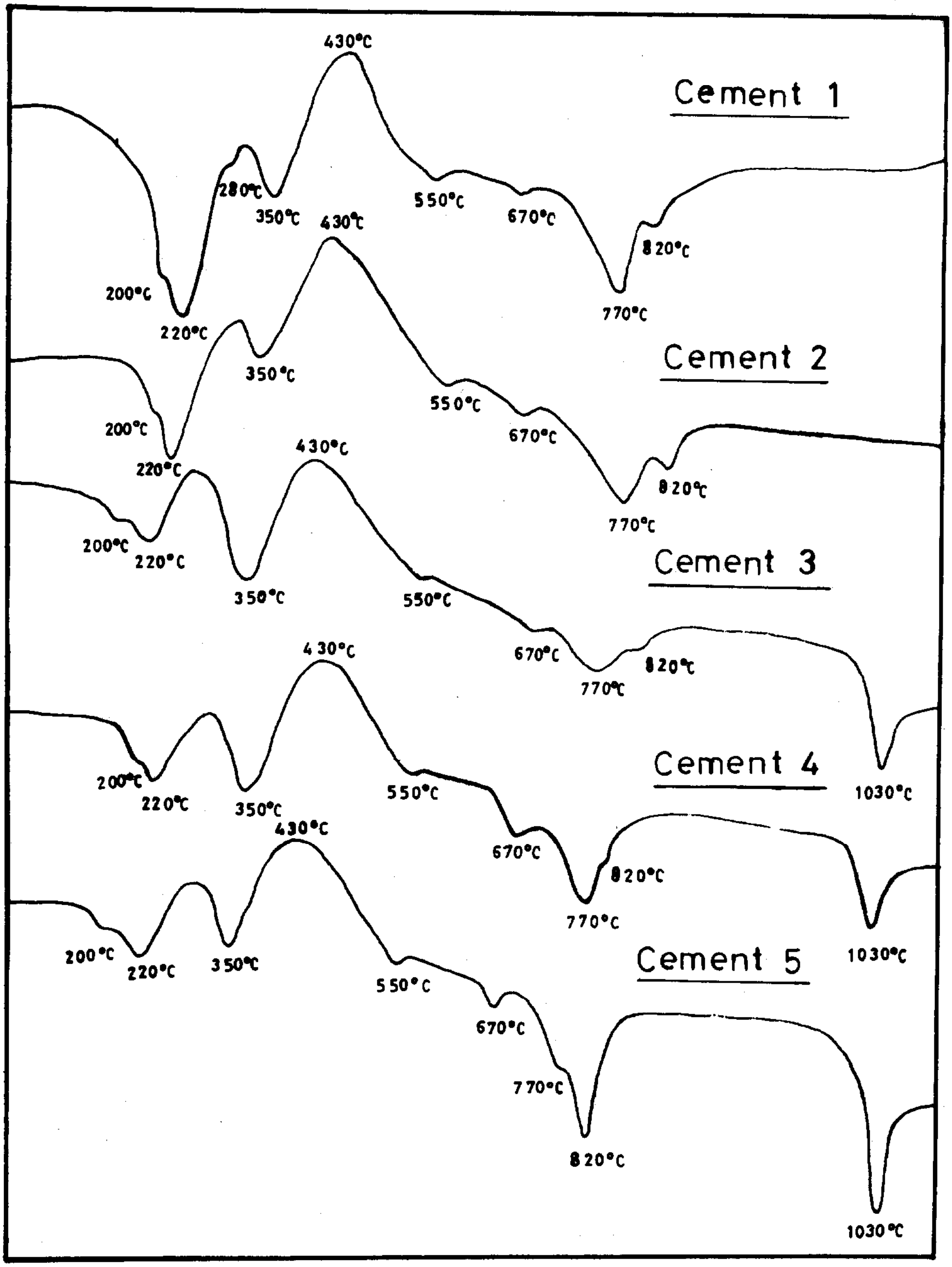

Fig. 3. DTA curves of the hardened magnesiochrome cements (mixed with 30% $MgCl_2 \cdot 6H_2O$ solution).

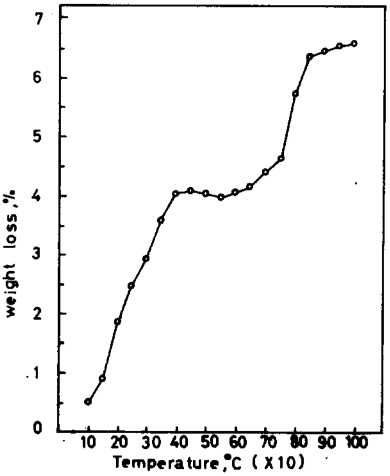

Fig. 4. TGA curve of cement 1.

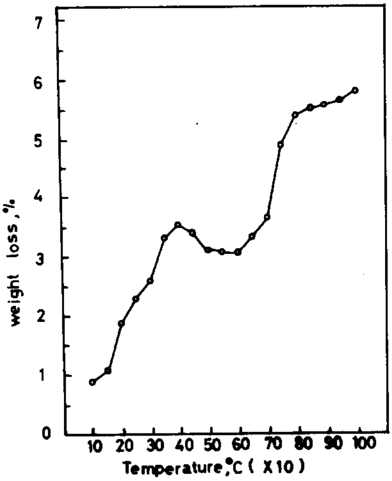

Fig. 5. TGA curve of cement 2.

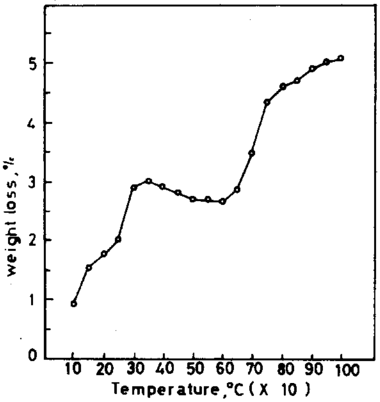

Fig. 6. TGA curve of cement 3.

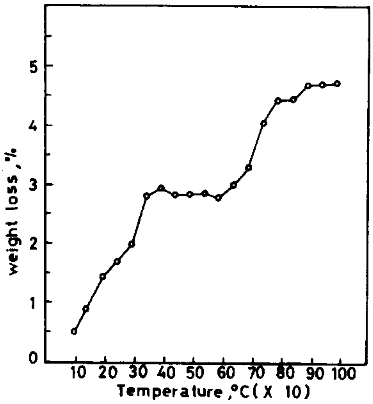

Fig. 7. TGA curve of cement 4.

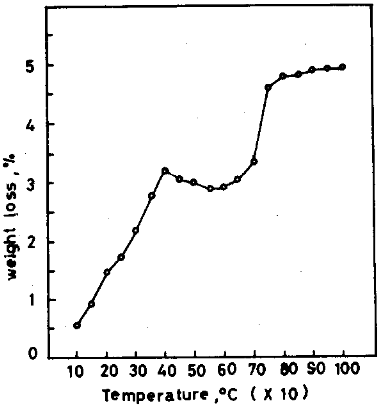

Fig. 8. TGA curve of cement 5.

Thermogravimetric analysis (TGA)

The thermogravimetric analysis curves of the investigated cements showed two stages of weight loss. The first stage came to an end at 400°C, and corresponds to the decomposition of magnesium-oxychloride, as well as the dehydration of Ca-chromate dihydrate and brucite [11,13,14,16–18]. The second stage of weight loss began at 550°C and came to an end at 900°C. It corresponds to the dehydration of portlandite as well as the decarbonization of magnesium- and calcium secondary carbonates [11,13,14]. The TGA curves obtained showed a depression in weight loss between 400 and 550°C. This weight loss depression was found to be shallow in the case of cement 1 (Fig. 4), and showed a remarkable increase in amplitude in the case of the other cements (Figs. 5–8). The weight gain corresponds to the combination of Ca-monochromite with lime and oxygen, and formation of Ca-chromate [15], which was confirmed with the noticeable development of the bright yellow chromate colour in samples heated to 600°C in separate experiments.

CONCLUSIONS

From the results obtained, the following conclusions can be made.

In both of the series of samples studied, the amounts of Ca-chromate dihydrate as well as secondary calcium carbonate were found to increase with increase of Ca-chromate chromite. Above 30% of the latter constituent, the dissociation of Ca-chromate at 1030°C became detectable by DTA. On the other hand, the amount of brucite and secondary Mg-carbonate increased with increase of periclase content.

Mixing with 30% $MgCl_2 \cdot 6\ H_2O$ solution instead of water resulted in the formation of magnesium oxychloride, which is known to improve the binding properties. In general, the hydration process was found to be noticeably enhanced. This is clear from the increase in amplitude of brucite and combined carbonates endotherms, in addition to the appearance of secondary Mg-carbonate peaks. The enhanced hydration was accompanied by an improvement in degree of crystallinity of the hydration products, which was clear from the relative sharpness of the DTA peaks.

In spite of the relatively complex nature of the studied cements, valuable data could be obtained. TGA was helpful in detecting the oxidation of Ca-monochromite into Ca-chromate between 400 and 550°C. The DTA exothermic peak corresponding to this reaction was defined as occurring at 430°C. The lowest temperature for this reaction was previously reported as 500°C. Another interesting point declared by DTA was the dissociation of the Ca-chromate at 1030°C. Through this process the Ca-chromate loses oxygen, and a limited amount of liquid, together with the highly refractory compound Ca-monochromite are formed.

It seems worthy, and meanwhile interesting, to follow up the influence of these thermal alterations in mineral constitution on technological properties of the hardened cements. This will be the subject of a further study.

REFERENCES

1 W.F. Ford and W.J. Rees, Trans. Br. Ceram. Soc., 48 (1949) 291.
2 P.P. Budnikov and E.A. El-Rafei, Dokl. Akad. Nauk S.S.S.R., 150 (1963) 1315.
3 P.P. Budnikov and E.A. El-Rafei, Proc. 7th Conf. Silicate Ind., Budapest, 1963.
4 P.P. Budnikov and E.A. El-Rafei, Epitoanyag, 16 (1964) 63.
5 M.R., Kamel, Tonind. Ztg., 103 (1979) 678.
6 M.R. Kamel, Ber. Dtsch. Keram. Ges., 57 (1980) 91.
7 R.S. Mathur, B. Rao and R. Singh, J. Sci. Ind. Res., Sect. A, 16 (1957) 28.
8 M. Koltermann and E. Kupzog, Ber. Dtsch. Keram. Ges., 43 (1966) 271.
9 W.L. De Keyser, Proc. 3rd Int. Symp. Chem. Cement, London, 1952.
10 M.R. Kamel and M. El-Sherbiny, Tonind. Ztg., 105 (1981) 396.
11 R.C. Weast (Ed.), Handbook of Chemistry and Physics. The Chemical Rubber Co., Cleveland Ohio, 47th edn., 1966.
12 H.F.W. Taylor, The Chemistry of Cements, Vol. 2, Academic Press, London, 1964.
13 L.G. Berg Introduction to Thermography, U.S.S.R. Academic Press, Moscow, 1961.
14 R.C. Mackenzie, Differential Thermal Analysis of Clays. Mineral Soc., London, 1957.
15 W.J. Ford and W.J. Rees, Trans. Br. Ceram. Soc., 47 (1948) 207.
16 A.G. Bergman and I.P. Virdov, Zh. Prikl. Khim., 31 (1958) 19.
17 I.P. Virdov and A.G. Bergman, Zh. Prikl. Khim., 32 (1959) 7.
18 N.F. Fedriv and N.S. Sadikov, Neorg. Mater., 2 (1966) 1124.