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Communication

Effect of barium on the formation of tricalcium silicate

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Abstract

The effect of barium carbonate on the kinetics of tricalcium silicate formation has been studied. Burnability study of mixes of calcium carbonate and quartz in 3:1 ratio and barium carbonate equivalent to 0.5 to 4% BaO by weight showed accelerated rate of clinkerisation through mineralising action. The addition of $BaCO_3$ significantly reduced the time and temperature of formation of C_3S. At 1450°C up to 1.85% BaO could be assimilated in forming solid solution of C_3S. With up to 2% BaO triclinic form and 4% BaO, monoclinic form of C_3S was stabilised. The solubility of BaO in C_3S at 1450°C was investigated using chemical analysis (estimation of free lime) and energy dispersive analysis of X-rays. The limit of solubility is found to be 1.85% (by weight) at 1450°C. Above the solubility limit, BaO formed Ba_3SiO_5 at 1450°C.

Keywords: Ca_3SiO_5; BaO; Miscibility; Free lime; Polymorph

1. Introduction

Barium present in cement raw materials, particularly clay and limestone, has been reported to have a mineralising effect on the kinetics of formation of clinker phases [1,2]. Thermal decomposition of the barium compounds, except barite, yields barium oxide, which influences the process of clinker preparation This results in the formation of new phases in the stabilisation of particular modifications of the usual clinker components and in the variation of the temperatures at which polymorphous transformations occur. This phenomenon also effects the setting and hardening processes; that is, the hydraulic properties of the cement minerals. Barium (Ba^{2+}) replaces calcium (Ca^{2+}) in all the minerals of clinker, except aluminoferrite [4]. Until 1970 the miscibility limit of BaO in C_3S was not known. Kurdowski and Wallast determined this to be 1.5 mole% (2.96 mass%) at 1600°C [5]. Appendino and Montorsi determined the solubility of BaO by finding the composition of the compound formed ($Ca_{1\cdot86}Ba_{0\cdot14}SiO_4$) at 1450°C by using rontgenograph, and they established that tricalcium silicate is not capable of dissolving quantities of BaO far in excess of 1 mole% (1.99% mass) [3].

In the present work, the miscibility of BaO in C_3S has been studied by estimating free lime and by EDAX in the completely fired specimens of pure C_3S and C_3S containing various amounts of BaO (0–4%), fired at 1450°C repeatedly, until free lime reduced to $<0.1\%$ in pure C_3S.

2. Methods

2.1. Preparation of specimens

Pure tricalcium silicate and its solid solutions with barium were made by solid-state reactions at 1450°C. The starting materials were analytical reagent grade calcium carbonate, quartz, and barium carbonate. Calcium carbonate and quartz in the stoichiometric ratio of 3:1 were ground to a fine powder and homogenised with various amounts of barium carbonate in anhydrous acetone to make specimens that had BaO from 0.5 to 4% (mass%). The dried mass was pressed into pellets and fired at 1450°C for 4 h. Free lime was estimated in the specimens. The sintered pellets were ground to pass a 63 μm sieve and were reformed into pellets and again fired at 1450°C for 4 h and room cooled to ~27°C. This process was repeated until the free lime was reduced to $<0.1\%$ in the pure C_3S.

2.2. Chemical analysis

Free lime was estimated in the specimens (pure and doped) using ethylene glycol method [6], and corrections were made for BaO_f [7] extracted in the process by using Atomic Absorption Spectrophotometer 2100 Perkin Elmer (German) model.

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Table 1
% BaO/% free lime

% BaO in C_3S	0	0.5	1	2	4
Estimated % CaO + % BaO	0.06	0.20	0.39	1.64	8.21
% BaO by AAS	Nil	Nil	Nil	0.14	1.95
% CaO = % BaO	Nil	Nil	Nil	0.05	0.71
Corrected % CaO	0.06	0.20	0.39	1.59	7.50
Theoretical % CaO = % BaO added (molar)	0.00	0.18	0.37	0.73	1.46

2.3. Electron microscopy

Scanning electron microscope (SEM) and energy dispersive analysis of X-rays (EDAX) studies were carried out on a Philips SEM 515 with EDAX PV 9900 (EDAX International, Inc., Prairie View, IL, USA) for the study of microstructural and morphological features, limit of BaO incorporation into C_3S, and its distribution.

2.4. X-ray diffraction studies

Rigaku Rad Max/III C model (Rigaku International Co., Tokyo, Japan) with Cu Kα radiation and Ni filter was used to study the formation of various C_3S polymorphs formed, among other features.

2.5. Burnability studies

Separate specimens of tricalcium silicate mixes were prepared containing 0.5, 1, 2, and 4% BaO as described earlier, but were fired at 1350, 1400, and 1450°C, giving a retention time of 1, 4, and 8 h. From the estimation of free lime, degree of conversion (α) of pure C_3S mix vis-à-vis BaO-doped mixes was calculated as seen in Eq. (1):

$$\alpha = \frac{CaO_t - CaO_f}{CaO_t} \cdot 100 \qquad (1)$$

3. Results and discussion

3.1. Chemical analysis

In the ethylene glycol method for the estimation of free lime, free BaO is also released and gets cotitrated with standard hydrochloric acid. Hence BaO_f was determined in the solution extracted by ethylene glycol, using AAS and equivalent percent CaO subtracted from the combined values of free CaO and BaO. Results are presented in Table 1.

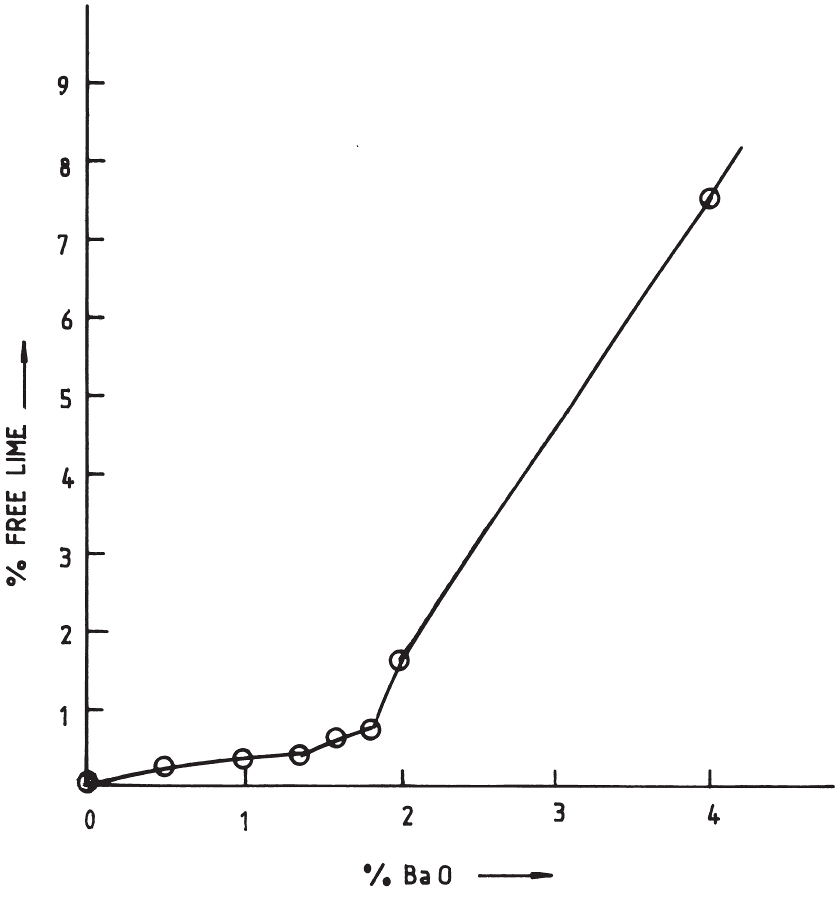

Fig. 1. Free lime/% BaO.

Results of free lime (Table 1) in the final products (when free lime reduced to $<0.1\%$ in pure C_3S) indicated that there was very little release of free lime with up to 1% BaO. In the specimens containing 2 and 4% BaO, there was a substantial release of free lime. This gives a rough idea that BaO substitutes CaO up to 1%, and beyond this there may be a decomposition of C_3S, releasing lime.

To know the exact amount of percent BaO between 1 and 2% that gives rise to the enormous release of free lime, further specimens of C_3S were made doped with 1.4, 1.6, and 1.8% BaO, as per the procedure already discussed. Free lime was estimated in these specimens. The results have been incorporated into Fig. 1 along with the results of Table 1. The results indicated that the free lime was approximately a CaO/BaO molar ratio of 1:1, with up to 1.8% BaO. Ba^{2+} ions simply replaced the Ca^{2+} ions with BaO up to 1.8% in C_3S. As soon as the addition of BaO exceeded 1.8%, there was a release of CaO (Fig. 1), showing that BaO substituted only up to 1.8% CaO. Beyond that there was decomposition of C_3S. This also proved that BaO went into C_3S solid solution up to 1.8% at 1450°C.

Kurdowski and Wollast [5] reported a miscibility of 1.5 mole% (2.96% by mass) at 1600°C using the same technique.

Boikova et al. [8] carried out investigations to obtain solid solutions of $3CaOSiO_2$ with $3BaOSiO_2$ at 1500°C. It was reported that samples with 1 wt% Ba_3S and more contained C_2S and uncombined CaO. It was concluded that solid solutions can therefore contain less than 1 wt% Ba_3S (%BaO = 0.88 by weight).

3.2. Electron microscopy

The microstructural and morphological features of the tricalcium silicate samples doped with various concentrations of BaO (0.5, 1, 1.8, 2, and 4%) were analyzed under a scanning electron microscope and EDAX, including elec-

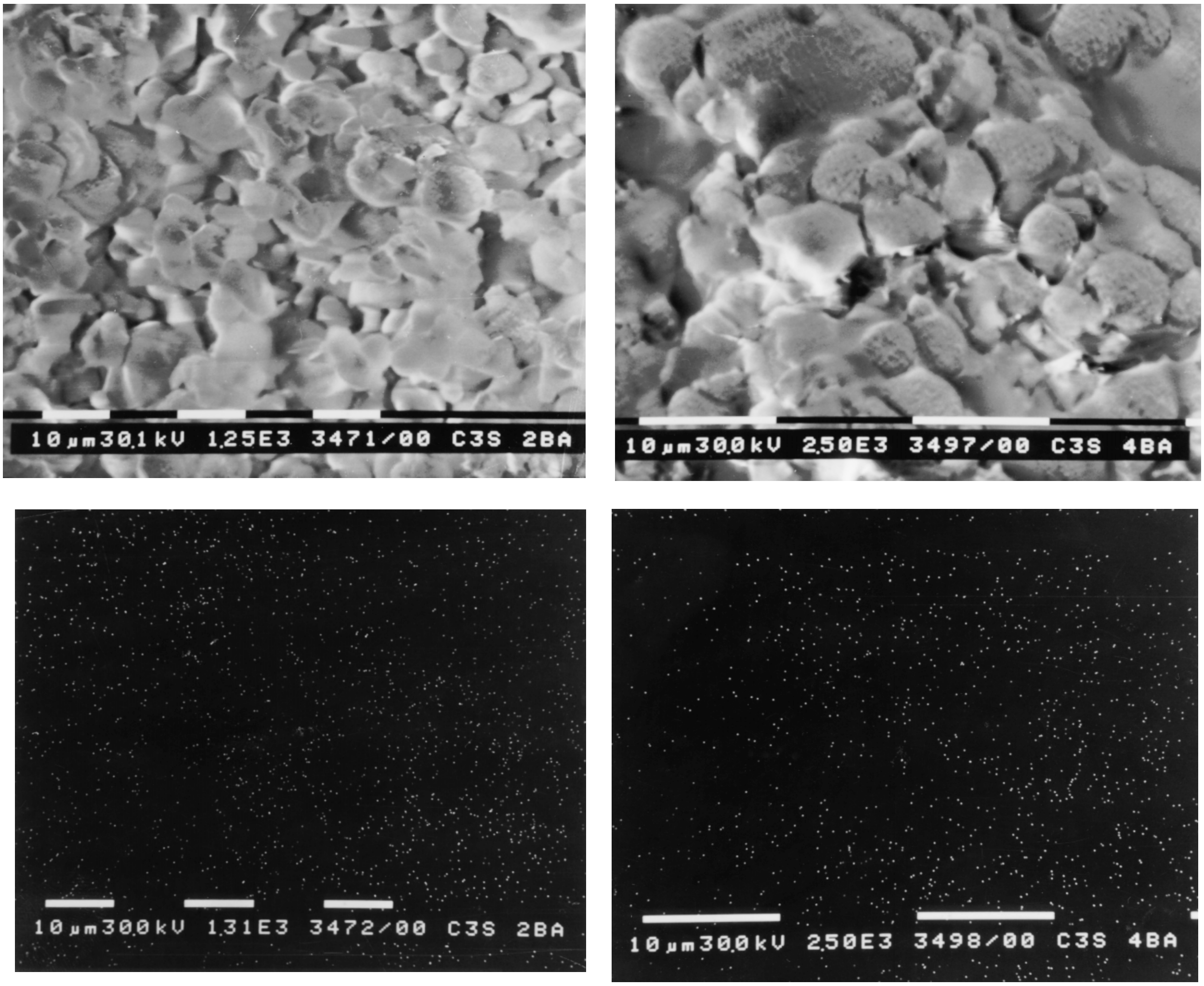

Fig. 2. Distribution of Ba.

Table 2
Miscibility of BaO in C_3S

This study, 1450°C	Appendino and Montorsi [3], 1450°C	Kurdowski and Wollast [5], 1600°C
1.85%	1.99%	2.96%

tron probe X-ray mapping, to determine the distribution of Ba. The samples doped with Ba did not show any improvement of C_3S crystal size as compared with that of pure C_3S.

Kurdowski [9] reported that barium does not influence the dimensions of alite crystals. However, Mullick et al. [10] reported improvement in crystal morphology and microstructure of clinkers containing barite.

Specimens having up to 1.8% BaO showed only the presence of C_3S. The specimen with 2% BaO showed mainly C_3S, and a very small amount of C_2S. In the specimen with 4% BaO, C_3S, C_2S, and CaO_f were present.

The elemental distribution for Ba X-ray mapping indicated an even distribution of Ba in the tricalcium-silicate up to 2%. Beyond 2% a substantial amount of Ba was located in the C_2S and interstitial zone. Micrographs are presented in Fig. 2.

EDAX analysis showed C_3S to contain up to 1.85% BaO at 1450°C (average of five point counts in each frame for 10 frames). This result is close to the value obtained by chemical analysis. The formation of any barium compounds could not be detected, probably because of the small amount of these compounds, although the presence of barium compound Ba_3SiO_5 was detected by X-ray diffraction. Miscibility of BaO in C_3S as reported by various authors is indicated in Table 2.

3.3. Burnability studies

Specimens (C_3S pure, 0.5, 1, 2, and 4% BaO) were fired at 1350, 1400, and 1450°C, maintaining a retention time of 1 h. Free lime was estimated. Results (Fig. 3) showed that BaO exerted a mineralising effect on the lime silica reaction up to 2% only, at 1450°C, causing the free lime content to be less than that without BaO addition. Fig. 3 shows that a concentration of 0.5% BaO brought down the free lime to the lowest value at 1450°C.

Free lime was also estimated in the specimens fired for 4 and 8 h at 1450°C. Degree of conversion was estimated from the values of free lime. Results are reported in Fig. 4. Results indicated that degree of conversion was maximum at the concentration of 0.5%. With the addition of 0.5% BaO, 96% degree of conversion was obtained by firing for 4 h

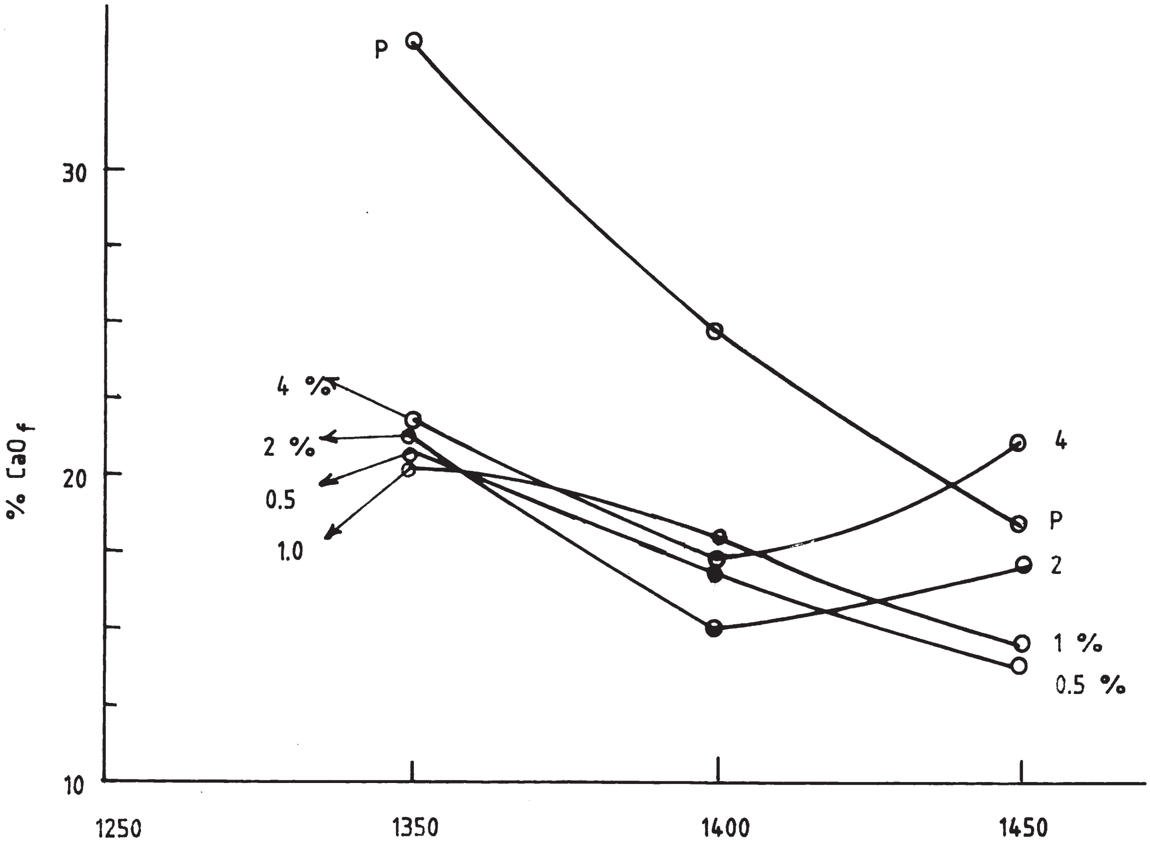

Fig. 3. % free lime/temperature °C.

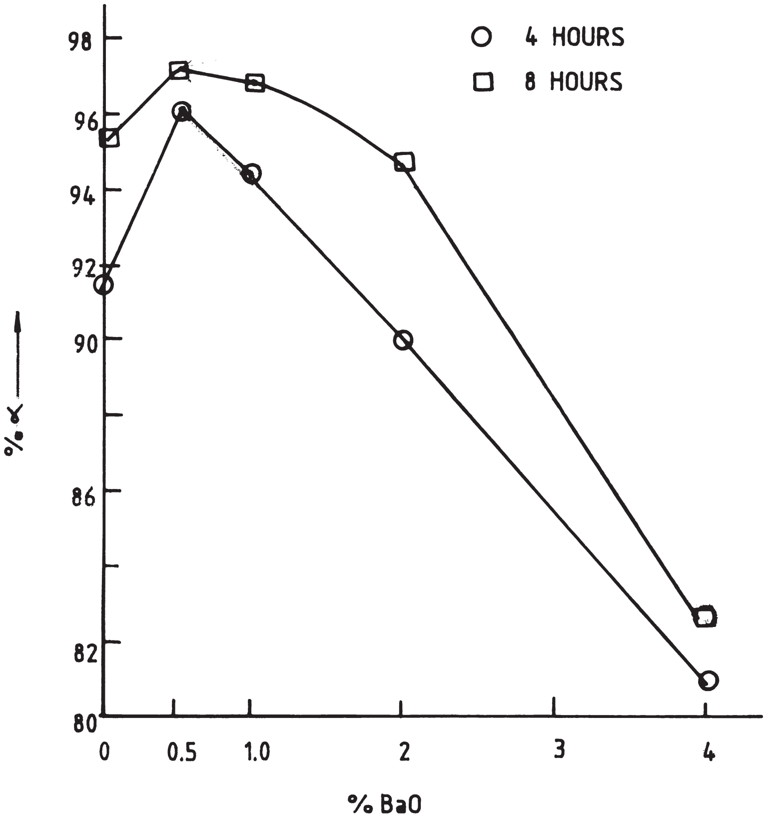

Fig. 4. Degree of conversion.

at 1450°C. The specimen without BaO addition produced almost the same degree of conversion in 8 h of firing at the same temperature (Fig. 4).

3.4. XRD studies

Solid solutions of foreign ions in C_3S caused a slight change in the unit cell dimensions and also caused a lowering of the temperature at which polymorphic changes occur [11]. Nurse [12] observed that there is good evidence that this polymorphic stabilisation affects the cementing power of C_3S, as well as its reactivity.

The introduction of Ba^{2+} ions into C_3S caused considerable changes in its structure, because of the big difference in the ionic radii of the Ba^{2+} and Ca^{2+} (1.43 and 1.06 Å, respectively) [5] Polymorphs of C_3S as detected in the specimens containing 0.5, 1, 2, and 4% BaO are presented in Table 3, in comparison with the work reported by other authors.

Kurdowski and Wollast's findings [5] indicated that the addition of BaO in the range of 0.1 to 3.45% (by weight) successively stabilised modifications T_1, T_{11}, T_{111}, and M_{II}. This was a rare case of obtaining T_{111} form at room temperature. Appendino and Montorsi reported that in the case of solid solutions of C_3S, the modification T_{11} generally tended to become transferred directly into monoclinic M_1 [3]. The same result was observed in this study also. Specimens with 4 and 2% BaO exhibited C_2S and free CaO (Fig. 5). The more barium present in the specimen, the more C_2S and free lime present in the products. Specimens with 2 and 4% BaO showed the presence of $3BaOSiO_2$. In the specimen with 4% BaO, the peaks indicating Ba_3S were very sharp. Peaks marked as 2 in Fig. 5 (having *d* values 3.12, 3.06, and 2.463 Å, respectively) are attributed to the presence of Ba_3SiO_5.

4. Conclusions

Up to 0.5% BaO by weight at 1450°C exerted the maximum mineralising action on C_3S formation. BaO went into solid solution of C_3S up to 1.85% at 1450°C. Up to 2% BaO, triclinic form and with 4% monoclinic form of C_3S was stabilised. Above the misicibility limit (i.e., 1.85% BaO (by weight) barium forms Ba_3SiO_5. Introduction of BaO more than 1.80% led to the decomposition of C_3S into C_2S and CaO.

Table 3
Polymorphs of C_3S/% BaO

This study, 1450°C	Appendino and Montorsi [3], 1450°C	Kurdowski and Wollast [5], 1600°C
C_3S pure T_1	C_3S pure T_1	C_3S pure T
C_3S 0.5% BaO T_1	–	C_3S 0.1–0.2% T_1
C_3S 1% BaO T_1	C_3S 1% T_1	C_3S 1% T_{11}
C_3S 2% BaO T_{11}	C_3S 1.99% T_{11}	C_3S 1.99% T_{111}
C_3S 4% BaO M_1	C_3S 3.96% T_{11}	C_3S 2.09–3.45% M_{11}

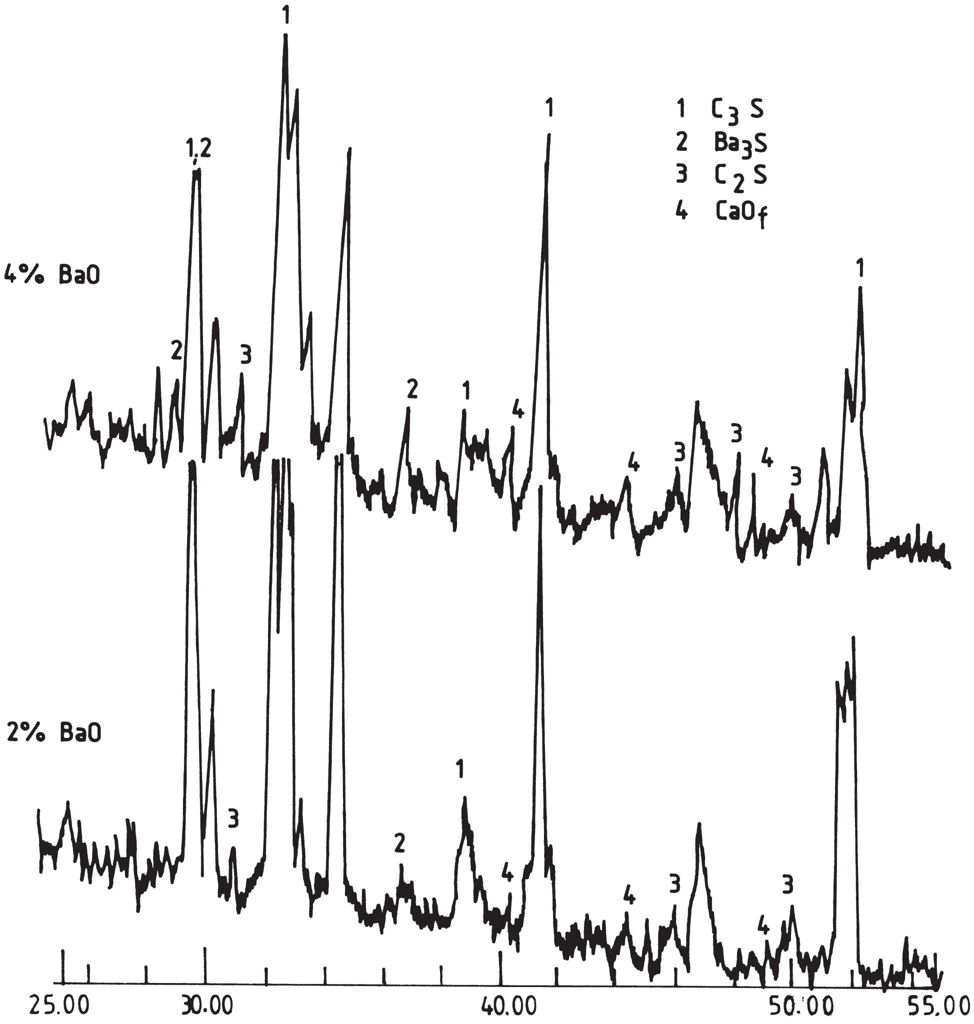

Fig. 5. XRD of C_3S with 4 and 2% BaO.

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