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Characterization of Blue Compounds Produced from Interaction between Cobalt Oxide and Kaolin Ore in Presence of Sodium Carbonate at Elevated Temperatures

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The reactions in ternary mixtures of sodium carbonate, hydrated cobalt chloride and kaolin at 1000° and 1300°C were examined by X-ray diffraction patterns and diffuse reflectance spectrometry. The effect of addition of different quantities of sodium carbonate to kaolin on the release of silica, alumina and some sodium aluminosilicate compounds such as mullite, nepheline, carneigieite (low form) and natrodavyne (high form) was investigated.

The factors which affect the formation of blue compounds such as cobalt aluminate, cobalt silicate and sodium cobaltate are discussed in the light of results obtained from both X-ray and diffuse reflectance spectrometry.

INTRODUCTION

Several studies were carried out on the solid state reactions between kaolin and sodium carbonate with different molar ratios at elevated temperatures.[1–4] Such studies describe and establish the identity and ranges of stability of various alkali silicates and aluminosilicates containing K_2O and/or Na_2O such as nepheline, carneigieite, kalsilite and kliophelite. However few studies[5–9] were done on the characterization of the blue coloured compound ($CoAl_2O_4$) which develops as a result of interaction between kaolin and cobalt oxide but most of them appeared in the form of patents[6–9]. The intensity of the resulted blue colour in such a study is only light which prevents its practical use as a pigment. So it is tried to develop a more intense colour suitable for application by addition of sodium carbonate to the reaction mixture which is composed of hydrated cobalt chloride and kaolin and roasting of them at 1000° and 1300°C. Bearing this in mind the present investigation is devoted to search for the factors which affect the developing of the intense blue colour by characterization of reaction product with different spectroscopic methods.

EXPERIMENTAL

(a) Materials

The starting materials, sodium carbonate and hydrated cobalt chloride were of

AnalaR grade and obtained from BDH chemicals. They were analyzed by the usual methods of analysis, whereas kaolin ore which was obtained from Sainai Peninsula, Egypt, was analyzed as mentioned previously[10]. The results of its chemical analysis are 47.1, 36.8, 0.6, 0.1, 0.9, 0.3, 0.06, 0.01 and 0.6% for SiO_2, Al_2O_3, Fe_2O_3, TiO_2, K_2O, Na_2O, CaO, MgO and Cl^- respectively.

(b) Reaction Mixtures

Kaolin—Na_2CO_3

A series of mixtures of kaolin and sodium carbonate with molar ratios (with respect to $Al_2O_3:Na_2O$) of 16:1 (I), 8:1 (II), 4:1 (III), 2:1 (IV), 1:1 (V), 1:1.5 (VI), 1:2 (VII) were prepared by mixing of the starting materials, homogenizing, grinding and sieving it to the desired particle size (–50 μ) were heated at 1000° and 1300°C.

Kaolin-Na_2CO_3—$CoCl_2{\cdot}6H_2O$

The same procedure as used for the preparation of the reaction mixtures (I–VII) was carried out after addition of hydrated cobaltous chloride ($CoCl_2{\cdot}6H_2O$) to achieve the desired molar ratios between Al_2O_3 and CoO (1 : 0.13), provided that every one mole of the cobalt salt produces one mole of CoO upon heating at 1000° and 1300°C. Additional two mixtures designated I* and III* were also prepared where the ratios between Al_2O_3, Na_2O and CoO amount to 6:1:0.13 and 3:1:0.13 respectively.

The reactions were carried out at 1000°C and 1300°C for 48 h where the temperature of the furnace is raised gradually from room temperature to the desired temperature with a rate equal 5°C/min. whereas the heated samples were cooled to the room temparature with a rate equal to *ca.* 25°C/min.

Visible-UV diffuse reflectance spectra and X-ray diffraction patterns were carried out as described previously[11]

RESULTS AND DISCUSSION

Before discussing the interactions which may have been taken place in ternary mixtures of sodium carbonate, hydrated cobalt chloride and kaolin ore at different temperatures, it is useful to define the minor minerals which are in admixture with kaolinite mineral in the ore. It can be concluded from X-ray diffraction patterns and chemical analysis of the sample under investigation that it is composed of *ca.* 96% kaolinite and *ca.* 4% muscovite provided that all potassium found in the ore is present in the muscovite mineral. The chemical composition of the ore is presented in the experimental section.

Characterization of Reaction Products Between Kaolin Ore and Sodium Carbonate at 1000° and 1300°C.

(*a*) At 1000°C: On heating the kaolin ore the crystallinity of muscovite decreases considerably whereas the kaolinite mineral is transformed into crystalline α-quartz and amorphous phase. The amorphous phase is produced as a result of transformation[12–14] of crystalline kaolinite to metakaolinite and silicon spinel according to the following equations:

$$Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O \xrightarrow{500°C} Al_2O_3{\cdot}2SiO_2 + 2H_2O \qquad (1)$$

$$2[Al_2O_3{\cdot}2SiO_2] \xrightarrow{925°C} 2Al_2O_3{\cdot}3SiO_2 + SiO_2 \qquad (2)$$

On addition of sodium carbonate with a small quantity of kaolin (mixs. I and II) the relative intensities of diffraction lines of both muscovite and α-quartz decrease appreciably due to attack by reactive alkaline species produced from sodium carbonate (Fig. 1 and Table 1). It is assumed that this attack produces sodium metasilicate and amorphous alumina. The existence of the latter compound is verified from the identification of crystalline α-alumina in reaction products at 1300°C as we can see later. By further addition of sodium carbonate to kaolin (mix. II), a significant quantity of heat evolved as a result of formation of different reaction products assists in the transformation of unreacted metakaolinite and/or silicon spinel into 1 : 1 and 3 : 2 mullite (Fig. 1) which require higher temperatures for their formation[1–3] according to the following equations:

$$2[2Al_2O_3{\cdot}3SiO_2] \xrightarrow{1100°C} \underset{1:1\ \text{mullite type}}{3[Al_2O_3 \cdot 2SiO_2]} + Al_2O_3 \qquad (3)$$

$$3[Al_2O_3{\cdot}2SiO_2] \xrightarrow{>1400°C} \underset{(3:2\ \text{mullite type})}{3Al_2O_3{\cdot}2SiO_2} + 4SiO_2 \qquad (4)$$

TABLE 1
CRYSTALLINE REACTION PRODUCTS BETWEEN KAOLIN AND SODIUM CARBONATE AT 1000°C

Molar Ratio kaolin : Na_2CO_3	Mixture	Crystalline Phases
1 : –	Plank	Muscovite, α-Quartz
16 : 1	I	Muscovite, α-Quartz
8 : 1	II	Muscovite, α-Quartz, Mullite
4 : 1	III	Muscovite, α-Quartz, Mullite, Nepheline
2 : 1	IV	α-Quartz, Nepheline, Carneigieite (high form)
1 : 1	V	Nepheline, Carneigieite, α-Alumina, $6NaAlSiO_4{\cdot}Na_2CO_3$
1 : 1.5	VI	Nepheline, α-Alumina, $3Na_2O{\cdot}2Al_2O_3{\cdot}4SiO_2$
1 : 2.0	VII	Nepheline, $3Na_2O{\cdot}2Al_2O_3{\cdot}4SiO_4$

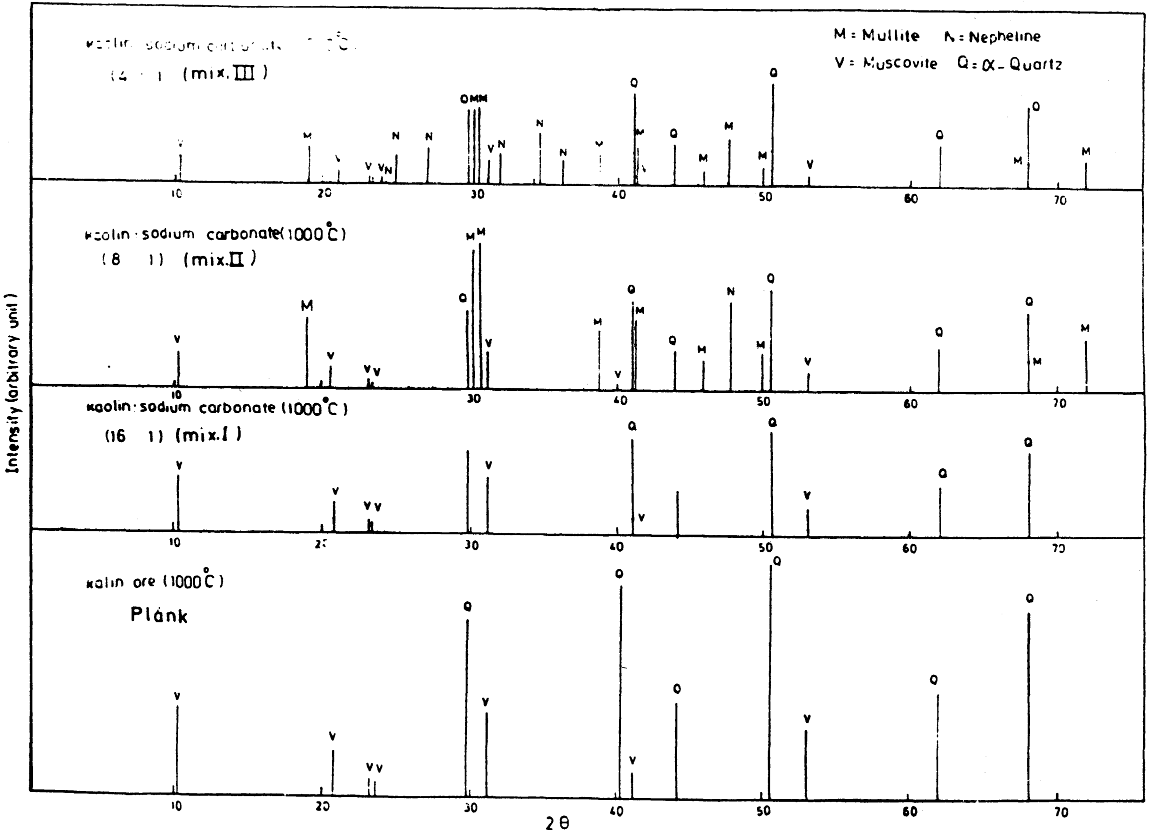

Fig. 1 X-ray diffraction patterns of kaolin ore and kaolin-Na_2CO_3 (mixtures I–III) heated at 1000°C

In case of mixture III (Fig. 1) the decrease in diffraction peaks of 3 : 2 mullite is associated with the appearance of diffraction patterns which are characteristic for the nepheline compound. This phenomenon can be explained on the hypothesis that mullite reacted with reactive alkaline species, formed from sodium carbonate, and produced nepheline, amorphous alumina and/or silica depending on the ratio between reactants according to the following equations:

$$2[Al_2O_3{\cdot}2SiO_2] + 2Na_2CO_3 \longrightarrow 4NaAlSiO_4 + 2CO_2 \qquad (5)$$

$$3Al_2O_3{\cdot}2SiO_2 + Na_2CO_3 \longrightarrow 2NaAlSiO_4 + 2Al_2O_3 + CO_2 \qquad (6)$$

When the ratio between Al_2O_3 (in kaolinite) and Na_2CO_3 reached 2 : 1 (mix. IV, Fig. 2 and Table 1) the carneigieite phase appeared where it is known that it is more stable at rich alkali environment.[15] On raising the ratio between alkali and aluminium oxide to 1 : 1 (mix. V) both mullite and α-quartz phases vanished completely whereas those of nepheline and carneigieite increased significantly and associated with appearance of the crystalline phase which has the molecular formula ($6NaAlSiO_4 \cdot Na_2CO_3$) as can be seen from Fig. 2 and Table 1. The summation equation for nepheline and/or carneigieite formation can be represented as follows:

$$Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O + Na_2CO_3 \longrightarrow 2NaAlSiO_4 + 2H_2O + CO_2 \qquad (7)$$

The variation of relative intensities of diffraction lines of nepheline and carneigieite with respect to each other in mixtures IV and V may be attributed to the fact that the relative proportions and degree of crystallinity of the two compounds depend primarily on both temperature and duration of heating during their formation. The same phenomenon was also detected and reported by Kubo *et al.*[14] On further increasing the ratio to 1 : 1.5 (mix. VI, Table 1) all carneigieite and some of nepheline were transformed into $3Na_2O{\cdot}2Al_2O_3{\cdot}4SiO_2$, where it was noticed that the transformation of carneigieite is faster than nepheline as appeared from the disappearance of its characteristic diffraction peaks.

On going to mixture VII (Table 1) the characteristic diffraction lines of α-Al_2O_3 vanished completely whereas those of nepheline and $3Na_2O{\cdot}2Al_2O_3{\cdot}4SiO_2$ decreased to variable extents. This phenomenon may be attributed to the fact that the last three components probably interact with each other to produce another silicate compound as appear from X-ray diffraction patterns of reaction products of a mixture composed of kaolin and sodium carbonate with a molar ratio 1 : 2.5 (unpublished results).

(*b*) **At 1300°C:** The investigation of different reaction products formed on heating at 1300°C indicates that the characteristic diffraction lines for muscovite vanished completely. At the same time the kaolin ore was transformed to 3 : 2 mullite. α-quartz and cristobalite (Fig. 3 and Table 2). The latter compound may result from diffusion of traces of some impurities into the silica crystallites.

The height of diffraction lines of the three compounds was decreased on further increasing carbonate content and associated with appearance of α-alumina in mixs. II–VII and of sodium aluminate in mixs. IV–VII (Table 2).

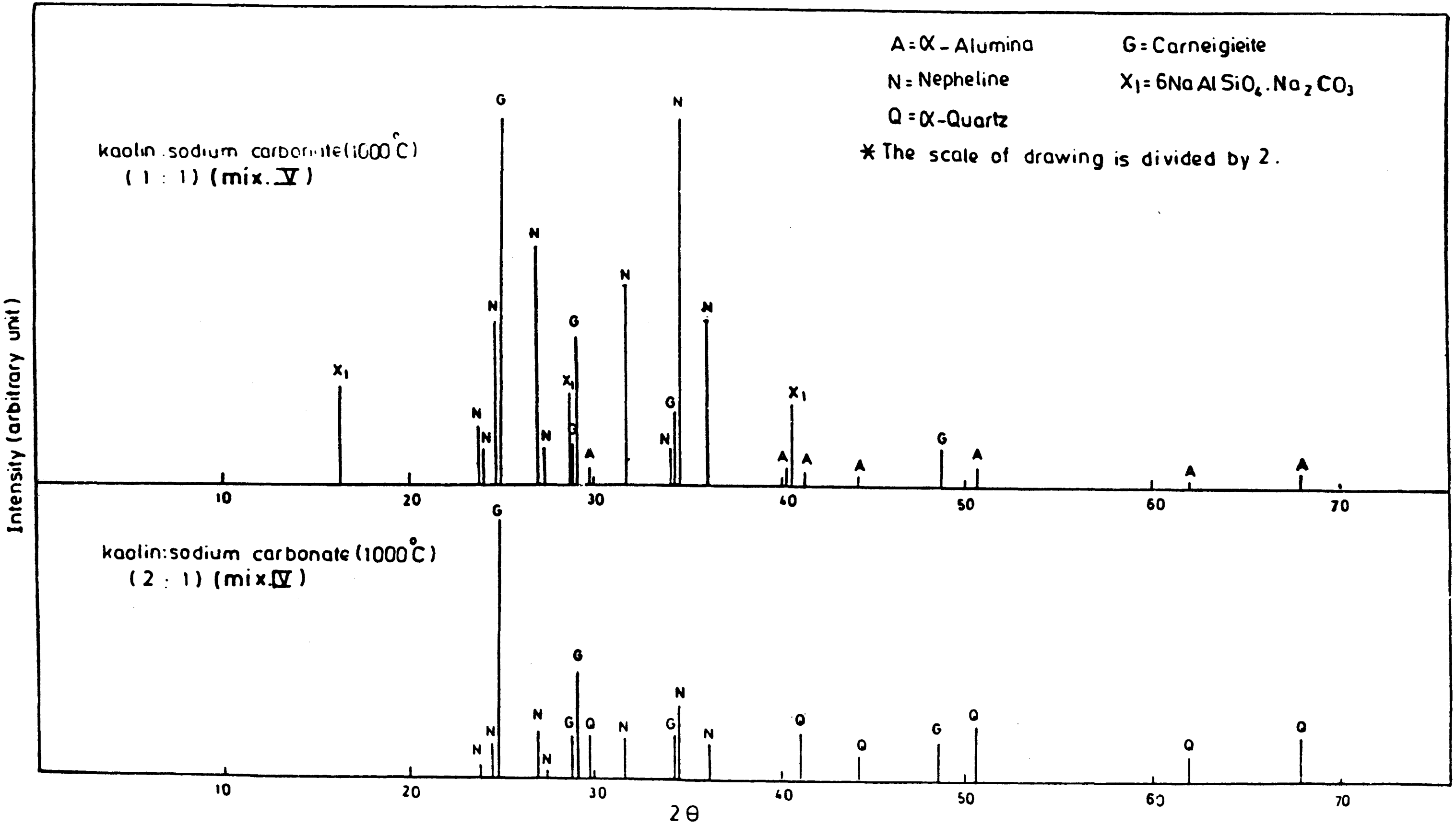

Fig. 2 X-ray diffraction patterns of kaolin-Na_2CO_3 (mixtures IV and V) heated at 1000°C

TABLE 2
CRYSTALLINE REACTION PRODUCTS BETWEEN KAOLIN AND SODIUM CARBONATE AT 1300°C

Molar Ratio Kaolin : Na_2CO_3	Mixture	Crystalline Phases
1 : –	Plank	α-Cristobaite, α-Quartz, Mullite
16 : 1	I	α-Cristobaite, α-Quartz, Mullite
8 : 1	II	α-Quartz, Mullite, α-Alumina
4 : 1	III	α-Quartz, Mullite, α-Alumina
2 : 1	IV	α-Quartz, mullite, α-Alumina, Sodium aluminate
1 : 1	V	α-Alumina, Sodium aluminate, Nepheline, Carneigieite, $3NaAlSiO_4 \cdot NaCl$
1 : 1.5	VI	α-Alumina, Sodium aluminate, Nepheline, Carneigieite, $3NaAlSiO_4 \cdot NaCl$
1 : 2.0	VII	α-Alumina, Sodium aluminate, Nepheline, Carneigieite, $3NaAlSiO_4 \cdot NaCl$

On increasing the ratio of Na_2CO_3 : kaolin to 1 : 1 (mix. V) the mullite phase vanished completely and associated with an appearance of nepheline, carneigieite, sodium aluminate and $3NaAlSiO_4 \cdot NaCl$*. The diffraction intensities of the last compound increased by increasing sodium carbonate ratio approaching 2 : 1 (mix. VII), whereas those characteristic of the first three compounds were decreased to different extents (Fig. 4). This phenomenon may be taken as an indication of the probable formation of another reaction products on going to higher ratios between Na_2O and Al_2O_3. The confirmation of such a phenomenon was gained from the results of unpublished results which clarified that further increasing of the ratio between reactants to 1 : 2.5 led to an appearance of other products different in their indices from that for the compounds mentioned before.

Characterization of Reaction Products of Kaolin—$CoCl_2 \cdot 6H_2O$ Interaction In Presence of Sodium Carbonate at 1000° and 1300°C

(*a*) **At 1000°C:** On heating a mixture of kaolin and cobalt oxide (produced from cobaltous chloride decomposition) with a molar ratio of 1 : 0.13 at 1000°C, it produces a mixture of cobalt aluminate, mullite and α-quartz (Table 3). The formation of mullite at such relatively low temperature can be attributed to the flux effect of CoO and to the energy evolved during the formation of the other products on addition of sodium carbonate with different proportions to the mixture of kaolin and cobalt chloride. It was noticed that the intensity of diffraction peaks of cobalt aluminate increased by increasing sodium carbonate and associated by a decrease in α-quartz phase from one side and increase of mullite phase from the other side as can be seen from the results obtained from heating the mixtures I–III (Table 3).

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*The chlorine required for its formation was gained from the chloride species in the kaolin ore.

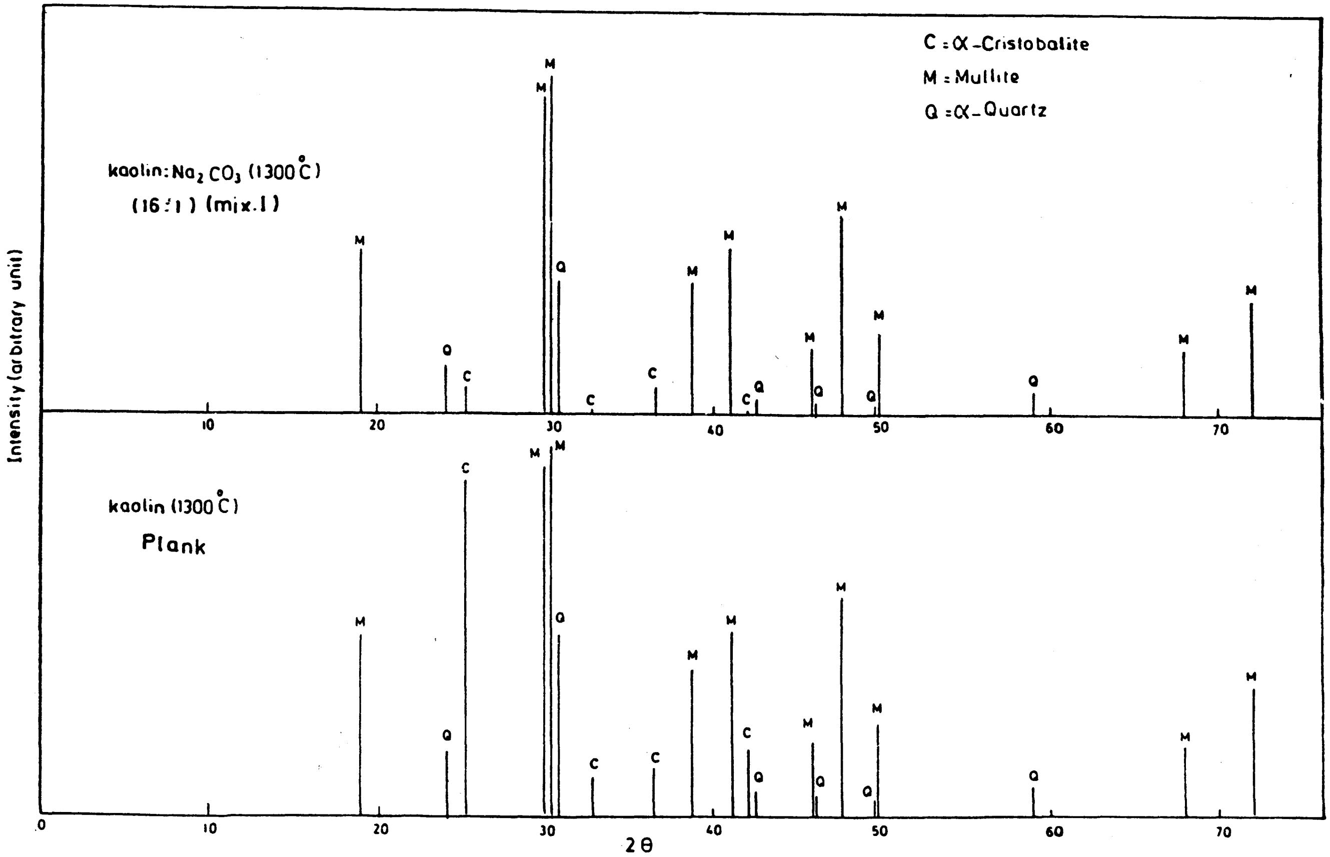

Fig. 3 X-ray diffraction patterns of kaolin ore and kaolin-Na_2CO_3 (Mixture 1) heated at 1300°C

TABLE 3
CRYSTALLINE REACTION PRODUCTS BETWEEN KAOLIN AND COBALT OXIDE IN PRESENCE OF SODIUM CARBONATE AT 1000°C

Molar Ratio Kaolin : Na_2CO_3 : CoO	Mixture	Crystalline Phases
1 : – : 0.13	Plank	α-Quartz, Mullite, Cobalt aluminate
16 : 1 : 0.13	I	α-Quartz, Mullite, Cobalt aluminate
8 : 1 : 0.13	II	α-Quartz, Mullite, Cobalt aluminate
4 : 1 : 0.13	III	α-Quartz, Mullite, Cobalt aluminate
2 : 1 : 0.13	IV	α-Quartz, Cobalt aluminate, Cobalt silicate
1 : 1 : 0.13	V	α-Quartz, Cobalt aluminate, Cobalt silicate, Nepheline, Carneigieite
1 : 1.5 : 0.13	VI	Cobalt aluminate, Cobalt silicate, Nepheline, $6NaAlSiO_4 \cdot Na_2CO_3$(XI), $3Na_2O \cdot 2Al_2O_3 \cdot 4SiO_2$(Y)
1 : 2.0 : 0.13	VII	Cobalt aluminate, Cobalt silicate, $3Na_2O_2Al_2O_3 \cdot 4SiO_2$, $3NaAlSiO_4 \cdot Na_2CO_3$ (Natrodavyne) (high form)

The increase in the degree of crystallinity of cobalt aluminate was also indicated from the increase of its absorption values in mixture III, compared with the plank sample (Fig. 5) where it shows its characteristic absorption peaks which are located at 478,549,586 and 630 nm[16]. It seems that the quantity of heat liberated from such reaction mixtures exhibits the increase of crystallinity of cobalt aluminate. On going to mixture IV (Fig. 4 and Table 3) it was noticed that the significant decrease in the heights of diffraction lines of α-quartz, cobalt aluminate was associated with disappearance of mullite phase from one side and appearance of cobalt silicate from the other side. The poor crystallinity of the last compound leads to the appearance of broad and short diffraction peaks which consequently appeared as short vertical lines upon representation as shown in Fig. 4. The confirmation of its presence is also gained from the electronic absorption spectra, where it appeared as a mixture of its spectra together with that of cobalt aluminate, taking into consideration that it is known that the locations of absorption maxima of cobalt silicate lie at *ca.* 492,520,578 and 751 nm.[16] In case of mixture V the interaction between mullite and sodium carbonate produces nepheline, carneigieite and leads to more crystallization of cobalt silicate as appeared from increase of its absorption spectra. The whole quantity of carneigieite together with high percentage of nepheline. are transformed to $3Na_2O \cdot 2Al_2O_3 \cdot 4SiO_2$(Y) and $6NaAlSiO_4 \cdot Na_2CO_3(X_1)$ in mixture VI and compounds (Y) and natrodavyne $3Na \cdot AlSiO_4 \cdot Na_2CO_3(X_2)$ in mixture VII. The last mentioned transformations may also lead to an increase of both quantity and degree of crystallinity of cobalt silicate which may be ascribed to the flux effect of sodium carbonate due to the energy evolved as a result of formation of the various reaction products. The increase of quantity and crystallinity of cobalt silicate was indicated from the pronounced increase in the values of absorption spectra of mixtures IV–VII as shown in Table 3. (Fig. 5)

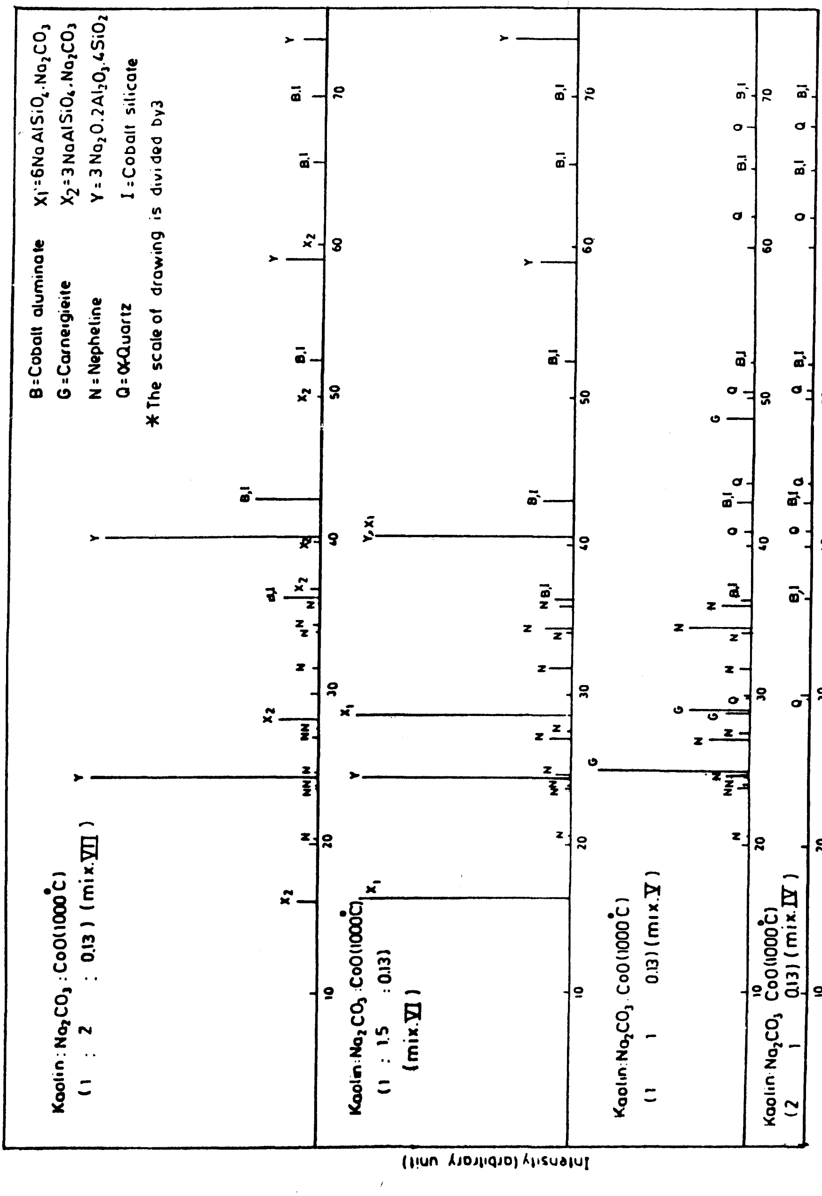

Fig. 4 X-ray diffraction patterns of mixtures of kaolin, Na_2CO_2 and CoO with different molar ratios heated at 1000°C, mixtures IV–VII.

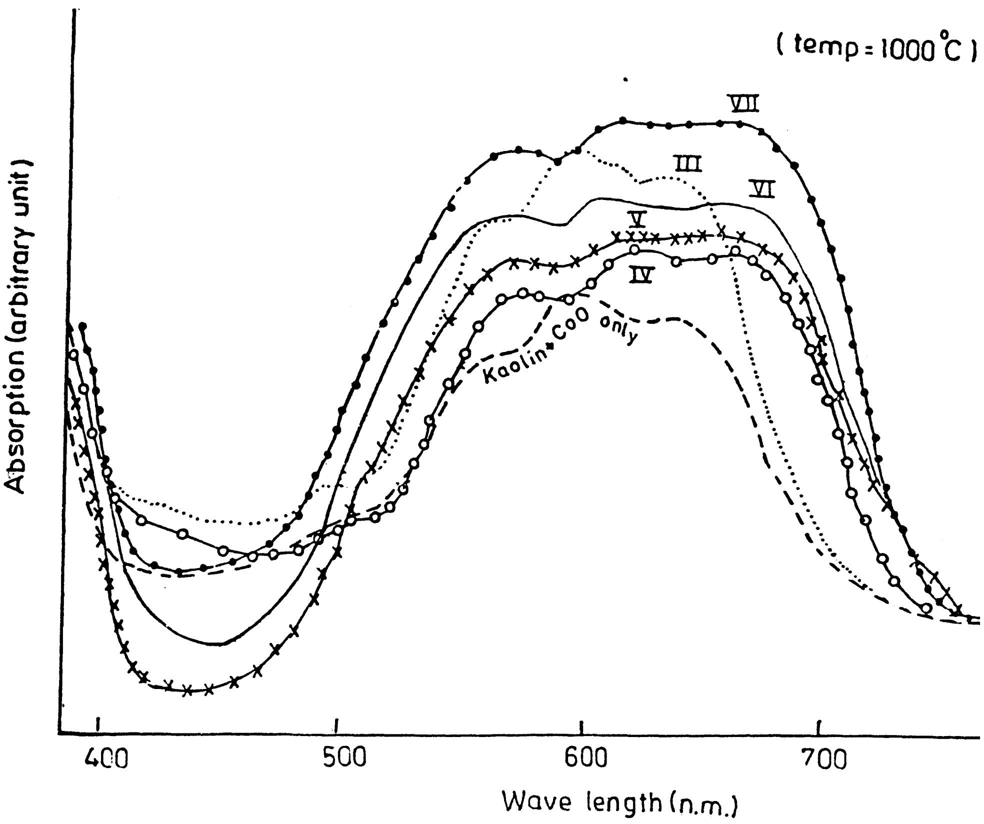

Fig. 5 Absorption spectra of reaction products of some mixtures of kaolin, Na_2CO_3 and CoO heated at 1000°C

***(b)* At 1300°C:** The reaction between kaolin and cobalt oxide produced from cobaltous chloride decomposition at 1300°C produce cristobalite, aluminate and silicate of cobalt together with mullite (Fig. 6 and Table 4) according to the following equation:

$$\begin{aligned} 5[Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O] + 4CoO &\xrightarrow{1300°C} Co_2SiO_4 + 2CoAl_2O_4 \\ &+ 3Al_2O_3 \cdot 2SiO_2 + 7SiO_2 + 10H_2O \qquad (8) \end{aligned}$$

On addition of sodium carbonate to reaction mixture which is composed of kaolin and cobalt oxide with different proportions it was noticed by inspection of Figs. 6 and 7 that the heights of diffraction lines of mullite and α-quartz gradually decreased with increasing contents of sodium carbonate in reaction mixtures whereas those characteristic for alumina increased appreciably in mixs. I–III* (Figs. 7, 8 and Table 4).

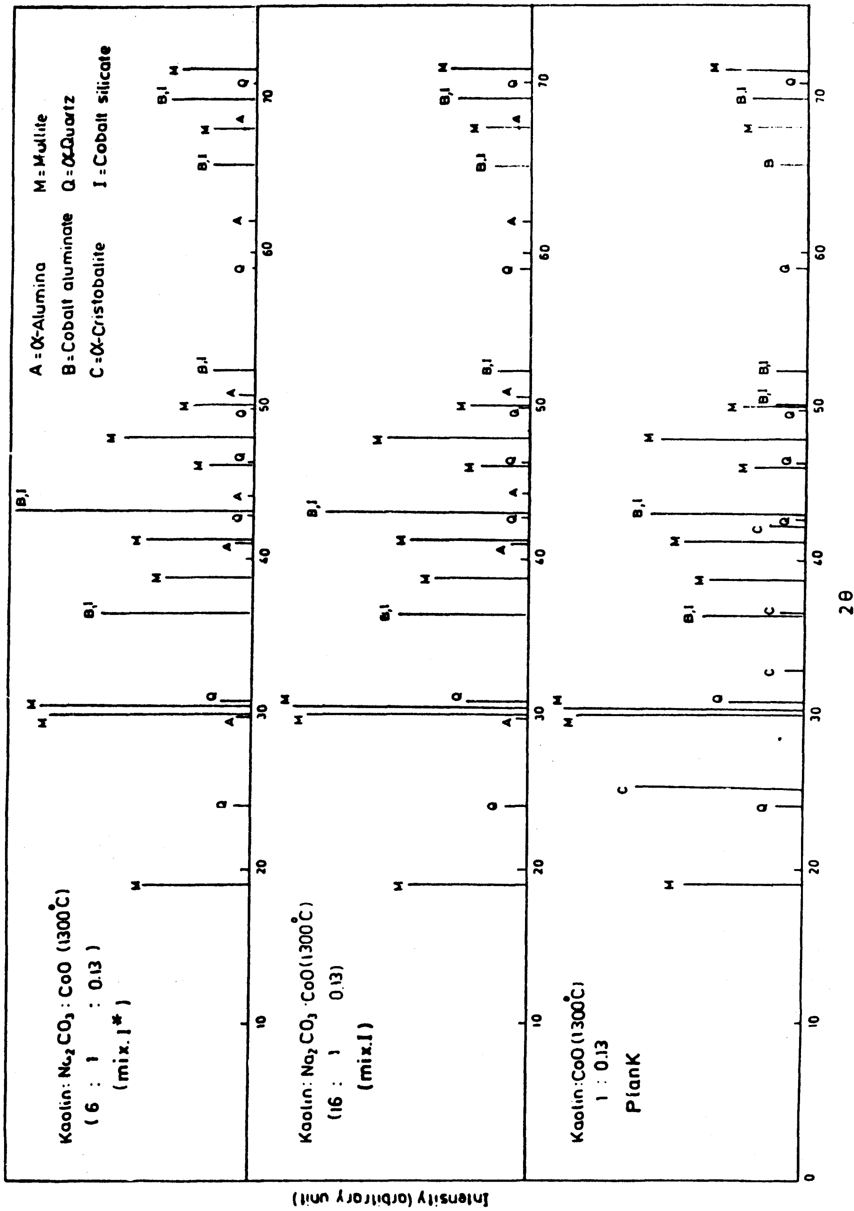

Fig. 6 X-ray diffraction patterns of ternary mixtures of kaolin: Na_2CO_3 and CoO with different molar ratios heated at 1300°C, plank and mixtures I and I*.

TABLE 4
CRYSTALLINE REACTION PRODUCTS BETWEEN KAOLIN AND COBALT OXIDE IN PRESENCE OF SODIUM CARBONATE AT 1300°C

Molar Ratio Kaolin : Na_2CO_3 : CoO	Mixture	Crystalline Phases
1 : – : 0.13	Plank	α-Quartz, Cristobalite, Cobalt aluminate, Cobalt silicate.
16 : 1 : 0.13	I	α-Quartz, Cobalt aluminate, Cobalt silicate. α-Alumina, Mullite
6 : 1 : 0.13	I*	α-Quartz, Mullite, Cobalt aluminate, Cobalt silicate, α-Alumina, Mullite
4 : 1 : 0.13	III	α-Quartz, Cobalt aluminate, Cobalt silicate, α-Alumina, Mullite
3 : 1 : 0.13	III*	α-Quartz, Mullite, Cobalt silicate, α-Alumina
2 : 1 : 0.13	IV	α-Quartz, Cobalt aluminate, Cobalt silicate, α-Alumina
1 : 1 ; 0.13	V	Cobalt aluminate, Cobalt silicate, Nepheline, Carneigieite
1 : 1.5 : 0.13	VI	Cobalt aluminate, Cobalt silicate, Carneigieite, Nepheline, Sodium aluminate, $3NaAlSiO_4 \cdot NaCl$
1 : 2 : 0.13	VII	Cobalt aluminate, Cobalt silicate, Carneigieite Nepheline, Sodium aluminate, $3NaAlSiO_4 \cdot NaCl$

On going to mixture IV (Fig 7) the mullite phase vanished completely and transformed to nepheline and carneigieite which appeared in a well crystallized form in addition to sodium aluminate in mixs. V–VII (Fig 8).

A significant quantity of $3NaAlSiO_4 \cdot NaCl$ is also formed in mixs. VI and VII. The increase in alkaline content in the last two mixtures led to formation of sodium cobaltate* as noticed from appearance of its characteristic diffraction lines in Fig. 8. It is noteworthy to mention that the heights of diffraction lines of cobalt aluminate and cobalt silicate, which have, nearly, the same peak positions, increase gradually by increasing sodium carbonate content in the reaction mixtures I–III (Figs. 6 and 7) due to increase in their degree of crystallinity which is associated with increase in their absorption values as can be seen from their electronic absorption spectra in Fig. 9. On the other hand the degree of crystallinity of both compounds decreases appreciably with increasing carbonate content in reaction mixtures III–VII. This phenomenon may be attributed to the fact that the quantity of heat liberated as a result of interaction between reactants in such mixtures is in excess so as to affect adversely the regularity of crystals of aluminate and silicate of cobalt and renders them less crystalline as can be seen from Figs. 7 and 8. This assumption is also indicated from the decrease in their electronic absorption values appearing in Fig. 9 where it is known that the crystalline material possesses more intense colour compared with that of amorphous or less crystalline ones.

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*The presence of it in the reaction products may lead to increase in the broadening of the absorption peaks characteristic for aluminate and silicate of cobalt.

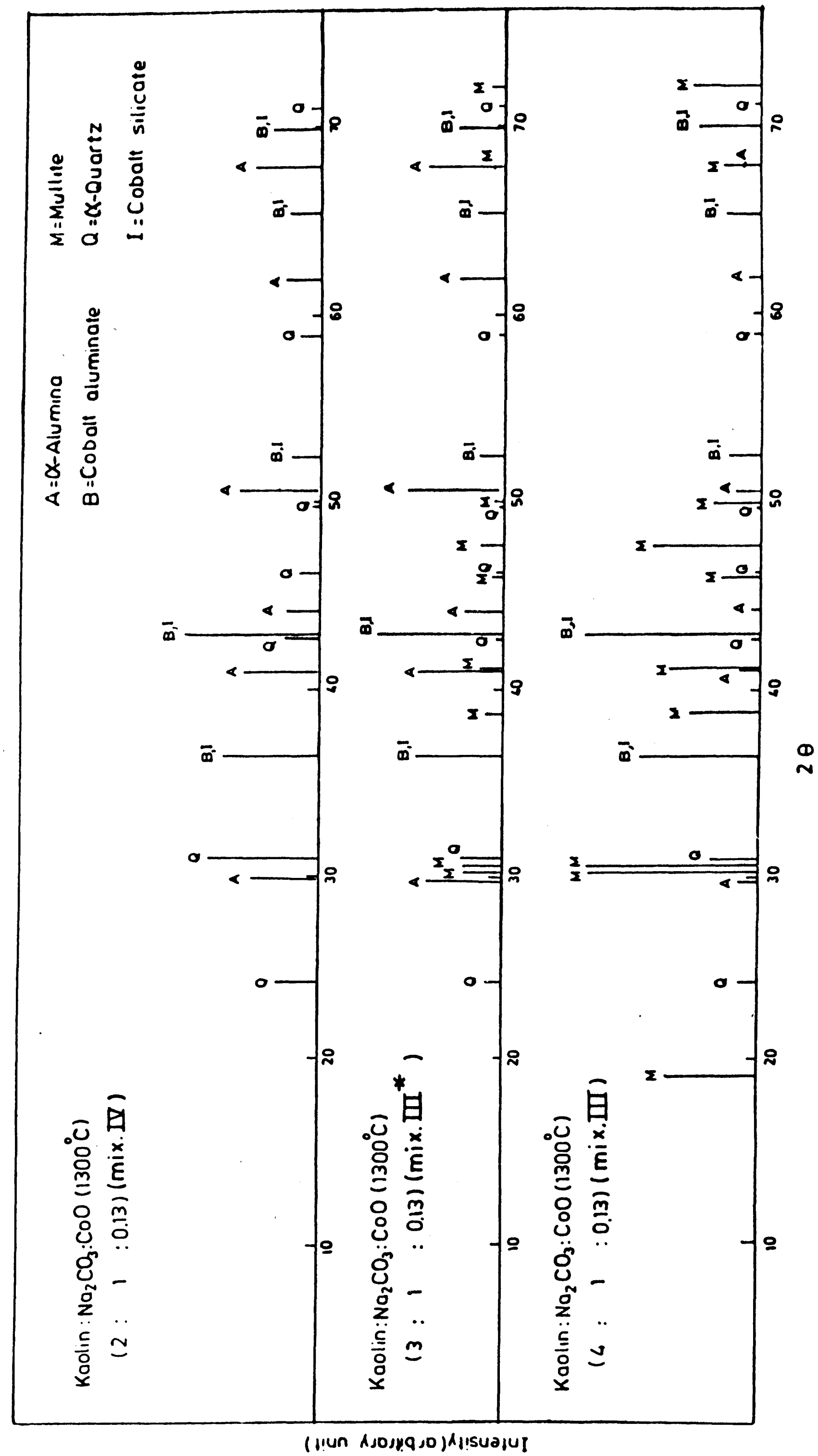

Fig. 7 X-ray diffraction patterns of ternary mixtures of kaolin, Na_2CO_3 and CoO with different molar ratios heated at 1300°C, mixtures III and IV.

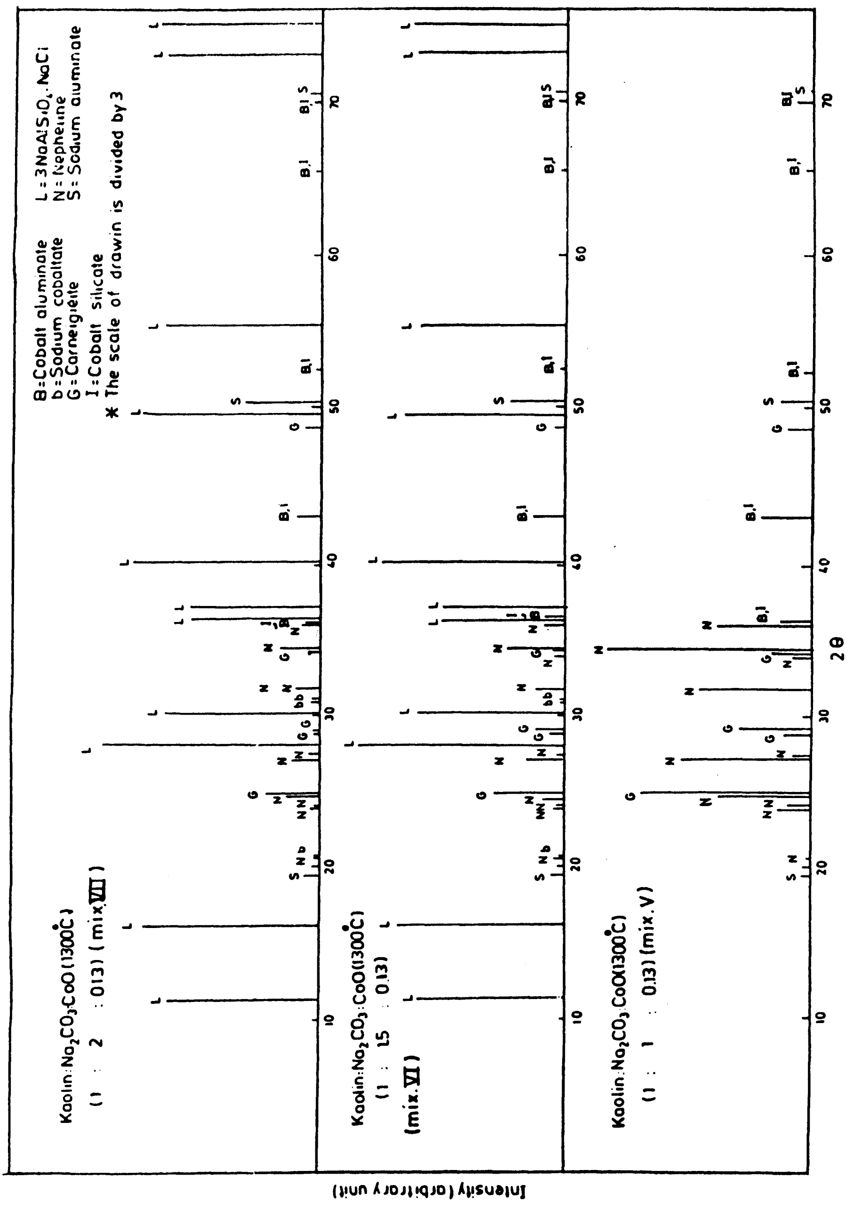

Fig. 8 X-ray diffraction patterns of ternary mixtures of kaolin, Na_2CO_3 and CoO with different molar ratios heated at 1300°C, mixtures V–VII.

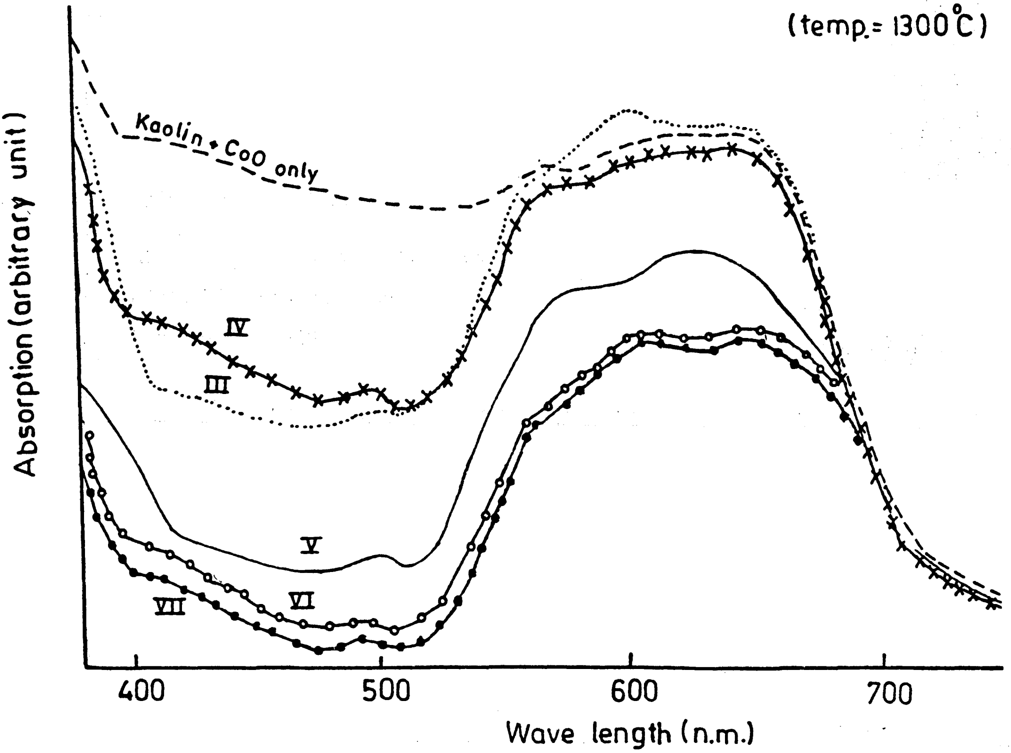

Fig. 9 Absorption spectra of reaction products of some mixtures of kaolin, Na_2CO_3 and CoO heated at 1300°C

Conclusion

1. The reaction between cobalt chloride and kaolin at 1000°C leads to formation of blue-coloured material which consists only of cobalt aluminate spinel.

2. The resulted blue compounds at 1300°C as a result of interaction of kaolin and the cobalt salt are composed of two colouring materials, namely, cobalt aluminate and cobalt silicate. They possess darker shades of colours with respect to reaction products at 1000°C which make it suitable for using as a heat resistant colouring pigment.

3. The addition of sodium carbonate to the reaction mixture, and heating at 1000°C, leads to formation of cobalt aluminate and cobalt silicate in case of mixtures which have sodium carbonate with a molar ratio equal to 1 : 1 or more with respect to kaolin. The formation of the last compound was enhanced by the heat liberated as a result of interaction between the reactants. It was found that the heat liberated is also suitable for crystal growth of cobalt silicate and hence leads to product with more intense colour suitable for practical application as a pigment.

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4. The addition of sodium carbonate to reaction mixture heated at 1300°C leads to formation of different reaction products which are associated with liberation of a different quantity of heat which adversely affect the degree of crystallinity of both cobalt aluminate and cobalt silicate in case of mixtures which are composed of kaolin and sodium carbonate with a molar ratio equals to 1 : 1 or higher with respect to kaolin.

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