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Use of by-pass cement on the production of sodium chromate from pellets containing chromite ore concentrate and soda ash

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ABSTRACT

The amount of by-pass cement produced from Egyptian Cement Companies is more than 10% of the total cement production. This dust is harmful on the health of human beings especially for those living near the company. It is known that the preparation and crushing of the raw materials for cement production is a highly expensive step. Accordingly, decreasing the amount of dust reduces the production cost of cement per ton. Many investigations were carried out to solve this problem by recycling this dust in alternative processes (e.g. use it in the production of cement, clay bricks, or as a fertilizer by mixing it with sewage water). Recycling it with raw materials can only be carried out in the wet process of cement production. Unfortunately, up till now these solutions has not yet been sufficient. In this investigation, a trial is made to use such dust as catalytic material in the production of sodium chromate. In this investigation, two feed materials consist of the chromite ore concentrate and soda ash with and without cement dust addition was firstly pelletized and the properties of the produced pellets were examined. The suitable pellets (from its mechanical properties point of view) were subjected to firing process at different temperatures, then the roasted pellets were dissolved in hot water and the sodium chromate was extracted from it. Also this paper studied the kinetics of formation of sodium chromate for both pellet types.

Keywords: Cement; Pellet; Chromite; Soda ash

1. INTRODUCTION

By-pass cement, which is designated as cement dust produced from different Egyptian cement companies, became a big problem in the last few years. The amount of this dust increased annually with increasing the demands for higher production of cement for country development and with the restricted environmental legislation the problem of such dust became more critical. To overcome such problem, the dust is introduced in an alternative useful industry like production of clay bricks, or as a fertilizer by mixing it with sewage water (Mohamed El-Menshawi, 2001). All trials to reuse such cement dust are not sufficient to consume all the rejected cement dust quantities, which represent about 10% of the total cement production.

Chromium compounds (such as sodium chromate) is regarded as a very important material according to its wide range of applications. Many industries use such compounds like, in metal finishing and corrosion control, in manufacturing of pigments and allied products, and in manufacturing of leather tanning and textiles.

There are many ways for obtaining such materials. One of them is the extraction of sodium chromate resulting from the firing of chromite ore in the presence of suitable amount of sodium carbonate.

Many investigations have been carried out to study the recovery degree of sodium chromate from chromite ore. From their results it can be concluded that there are many factors affecting the degree of sodium chromate recovery from chromite ore. These factors are:

- The roasting temperature.
- The roasting duration.
- Amount of sodium carbonate added.
- Types and amount of additives.

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El-Tawil *et al.* (1991) reported that the chromate recovery increased with increasing roasting temperature and maximum chromate recovery was achieved at 1100°C. Also, it was found that the chromate recovery increased with increasing the roasting duration.

Thomson *et al.* (1984) illustrated that when the chromite ore was roasted with 50% sodium carbonate at 750 – 900°C for < 40h, the yield of Cr in solution was ~83.6%. El-Darse *et al.* (2002), reported that the maximum chromic oxide recovery was achieved at 1000°C for a mixture of soda ash and chromite ore concentrate (Na_2CO_3 : Cr_2O_3 was 2.5 :1 mole ratio).

Other investigations have been carried out to study the effect of CaO or limestone as a catalyst on the degree of sodium chromate recovery from mixture of chromite ore and soda ash.

El-Tawil *et al.* (1991) found that the pellets containing CaO to Cr_2O_3 mole ratio of 2.4 yield a higher degree of chromate recovery whereas, the increase of CaO mole ratio beyond 2.4, no improvement in sodium chromate recovery was observed. Shalabi *et al.* (2001) found that the maximum chromic oxide recovery as sodium chromate was obtained when Cr_2O_3 : Na_2CO_3 : CaO were 1 : 2 : 2.5 mole ratio. El-Darse *et al.* (2002) and Abouzeid (2002) reported that the optimum chromic oxide recovery when briquetting a mixture of chromite ore concentrate, soda ash and cement dust was Cr_2O_3 : Na_2CO_3 : total CaO in cement dust was 1 : 2.5 : 3 mole ratio.

It can be noticed from the previous investigations that, many investigators have used the mixture of chromite ore and soda ash in the powder form in the production of chromic oxide. As a result of dust entrainment and formation (Ahmed, 2001), caused by using the mixture in the powder form leading to a failure of such process. While many of them have used the briquetting process for agglomeration of the feed materials prior to the roasting process. As a result of the mechanical unreliability of such process which leads to a high maintenance cost and low availability and the unsuitability for large scale production leading to the failure of this process (Ball, 1973). From such point of view, the application of the pelletization process on the agglomeration of such feed material is significant.

It is well known that the green pellets produced should have reasonable mechanical properties to withstand the transportation and handling. There are many factors affecting the mechanical properties of the green pellets, such as:

- The amount of water used during pelletization.
- The slope of the disc pelletizer.
- The residence time of the materials in the disc pelletizer.
- The particle size of the feed materials.
- The disc rotating speed.

As was mentioned before, the addition of CaO on the mixture of chromite ore with sodium carbonate was beneficial in obtaining a higher degree of sodium chromate recovery. From such point of view, the idea of using cement dust, which contains a reasonable amount of CaO instead of lime in such operation, was suggested.

Thus the aim of this investigation is to study the effect of different factors affecting the pelletization of a mixture of soda ash and chromite ore concentrate with and without by-pass cement. Also, the effect of roasting temperatures and roasting times on the sodium chromate recovery, as well as, the kinetics of sodium chromate production from such pellets were investigated.

2. EXPERIMENTAL

2.1. Material

The chromite ore concentrate used contains the following constituents: FeO = 10.2%, Cr_2O_3 = 48.8%, SiO_2 = 6.5%, CaO = 1.2%, Al_2O_3 = 15.2%, MgO = 16.8%, L.O.I = 0.65%. The soda ash used contains 90% Na_2CO_3. The by-pass cement has the following constituents Fe (as Fe_2O_3) = 2.35%, SiO_2 = 14%, CaO = 51% (16% as free CaO), Al_2O_3 = 3.5%, MgO = 1.8%, Na_2O = 3.18%, K_2O = 1.98%, Cl = 4.42% and L.O.I. = 9.5%.

2.2. Apparatus and experiments

To evaluate the effect of by-pass cement addition on both the mechanical properties of green pellets and the sodium chromate recovery, two feed materials were used:

1) Feed A: consist of a mixture of chromite ore concentrate with soda ash (Cr_2O_3 : Na_2CO_3 = 1 : 2.5 mole ratio), without by-pass cement addition.
2) Feed B: consists of chromite ore concentrate, soda ash and by-pass cement addition (Cr_2O_3 : Na_2CO_3 : CaO total in cement dust = 1 : 2.5 : 3 mole ratio).

The mixtures of the two different feeds were fed in a disc pelletizer of 40cm width and 10cm height.

The produced green pellets were subjected to mechanical properties tests (average drop number, and compressive strength).

The pellets, which are suitable to be charged in furnaces for the roasting stage, should have reasonable mechanical properties to withstand transportation and handling.

The green pellets produced were dried in a drying oven at 110°C, for 6h, to be sure that all water used during pelletization operation is evaporated. Then the dried pellets were subjected to the roasting stage in an open furnace for different temperatures and times. The sodium chromate recoveries as well as the kinetic of the reaction were studied.

Chromium recovery, % = (Wt of chromic oxide obtained from chemical analysis of dissolved sodium chromate in water resulted from fired pellets / Total wt of chromic oxide in dried pellets.)x100.

3. RESULTS AND DISCUSSION

3.1. Pelletization conditions

3.1.1. Effect of amount of water added on the mechanical properties of green pellets

The effect of water addition ranging from 30-34% of the total feed weight on the mechanical property of green pellets produced from both feeds A and B was studied. The following pelletization operation conditions were all kept constant throughout this experiments:

- Disc slope = 60°
- Disc rotating speed = 17rpm
- Residence time of material in the disc = 10min
- Feed particle size = -0.074mm

Table 1 shows the effect of water amount added on the mechanical properties of green pellets. From this Table, it can be seen that increasing water amount leads to increase both average drop number and compressive strength of green pellets up to a maximum at 31% in case of feed A, while the maximum was reached at 33% water in case of feed B. The average drop number and compressive strength decreased progressively beyond the maximum.

The increase in the mechanical properties of green pellets for both feeds with increasing water amount may be attributed to the fact that increasing water addition leads to increase in the coalescence mechanism between different constituent of the charge (Seddik *et al.*, 1978), and may be also attributed to the fact that increasing water amount added leads to increase in the number of liquid bridges between the particle of the charge (Meyer, 1980). Whereas the decrease of both the average drop number after it reach maximum at the optimum amount of water is attributed to the fact that increasing the water amount beyond the optimum water added leads to coats the pellets surface with a coherent film of water which neutralize the capillary effect (Ball, 1973).

From Table 1, it can also be noticed that the amount of water needed to reach the optimum mechanical properties of green pellets produced from feed B "in which by-pass cement was added" is much higher than in case of pellets produced from feed A, and this may be attributed to the fact that cement is designated as a hydrophilic material, accordingly, some of the water was taken by the cement.

Table 1
Effect of different parameters on the mechanical properties of green pellets

Variables	Degree of variation	Pellets containing by pass cement (Feed B)		Pellets free from by pass cement (Feed A)	
		Average drop number	Compressive strength, g/pellet	Average drop number	Compressive strength, g/pellet
Water amount, %	30	8.7	1018	54.3	7000
	31	9	1043	145	9700
	32	12	1100	120	8500
	33	15	1355	100	7500
	34	7	902.5	97.7	7500
Disc slope, °	50	5	975	120	5000
	55	10	1000	150	10000
	60	15	1355	145	9700
	65	9	1262.5	80	6000
	70	9	1212.5	50	5500
Residence time, min	5	7	1137.5	110	5000
	10	15	1355	150	10000
	15	9	1212.5	142	7500
	20	8	1080	139	7200
	25	7	1050	132	7000

3.1.2. Effect of disc slope on the mechanical properties of green pellets

The effect of disc slope on the mechanical properties of green pellets was studied. The following pelletization operation conditions were all kept constant throughout this experiment:

- Disc rotating speed = 17rpm
- Residence time of material in the disc = 10min
- Feed particle size = -0.074mm
- The water amount addition for feed A = 31%
- The water amount addition for feed B = 33%

Table 1, shows the effect of changing disc slope from 50 – 70° on the mechanical properties of green pellets. It was found that increasing of the disc slope from 50 to 70°, both average drop number and compressive strength of green pellets increased till it reached a maximum at 55° and 60° in case of pellets free and containing cement dust respectively, and then it decreased thereafter. This behavior may be attributed to the fact that there are two main angles on the disc pelletizer controlling the pelletization process. These two angles are the tilt angle of disc bottom and the dynamic angle of repose. The optimum pellet quality could be obtained when the dynamic angle of repose is lower than the tilt angle of disc bottom. These angles depend mainly on the type of material fed to the disc pelletizer (Meyer, 1980). The lower mechanical properties of pellets at disc angle lower than 55° in case of pellet free from cement dust and 60° in case of pellet containing cement dust may be attributed to the fact that the dynamic angle of repose is higher than the tilt angle of disc bottom. Whereas the decrease in pellets properties beyond 55°&60° in case of pellets free and containing cement dust is attributed to the fact that the charge would no longer be lifted by friction (Meyer, 1980).

3.1.3. Effect of residence time of feed material in the disc

The effect of different residence time of material in disc pelletizer on the properties of green pellets was studied. The following pelletization operation conditions were all kept constant throughout this experiment:

- Disc rotating speed = 17rpm
- Feed particle size = -0.074mm
- Disc slope for feed A = 55°
- Disc slope for feed B = 60°
- The water amount added for feed A = 31%
- The water amount added for feed B = 33%.

Table 1 shows the effect of changing residence time of pellets in the disc pelletizer ranging from 5–25min on the mechanical properties of green pellets. It was found that with increasing residence time of feed materials in the disc both average drop number and compressive strength of pellets produced from both feeds increased till it reaches maximum at 10min then it decreased thereafter. The increase of mechanical properties with increasing the residence time of material in the disc may be attributed to the growth of formed nuclei, while the decrease in the mechanical properties of pellets beyond 10min is attributed to the flushing of some moisture content during their growth (Ahmed, 1996).

3.2. Roasting of produced pellets

Pellets produced at the previous optimum pelletization condition, subjected to drying in a drier at 100°C for 6h. The dried pellets were roasted at different roasting temperatures (800-1000°C) for different roasting times and the results are shown in Figures 1 and 2. From these figures it can be concluded that at any fixed temperature the sodium chromate recovery increased with increasing the roasting time. Also, it can be concluded that at any fixed roasting time the increase in the roasting temperature leads to a significant increase in the sodium chromate recovery. The increase of sodium chromate recovery with increasing the roasting time at any fixed temperature may be attributed to the fact that the production of sodium chromate from chromic oxide by roasting process is carried out according to the following reaction:

$2Cr_2O_3 + 4Na_2CO_3 + 3O_2 = 4Na_2CrO_4 + 4CO_2$ (In the absence of cement dust, feed A) (1)

$2Cr_2O_3 + 4Na_2CO_3 + 4CaO + 3O_2 = 4Na_2CrO_4 + 4CaO + 4CO_2$ (In the presence of cement dust addition, feed B) (2)

This means that more time of the roasting process allows more oxygen to enter the reaction for production of sodium chromate. While the increase of sodium chromate recovery with increasing the roasting temperature at any fixed roasting time may be attributed to the fact that the increase of the temperature enhances the rates of various chemical and physical steps involved in the overall reaction process. The increase of temperature leads to an increase in the number of reacting molecules having excess activation energy, which subsequently leads to increase the reaction rate (Levenspinkl, 1981; Mc Cabe and Smith, 1976). Also, increasing temperature raises the rate of mass transfer of diffusion and the rate of adsorption of oxygen molecules leading to increase the reaction rate.

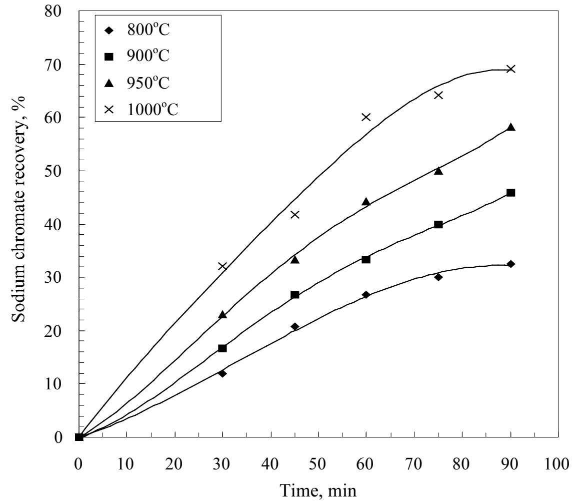

Figure 1. Effect of different temperature on sodium chromate recovery for pellets free from by-pass cement addition

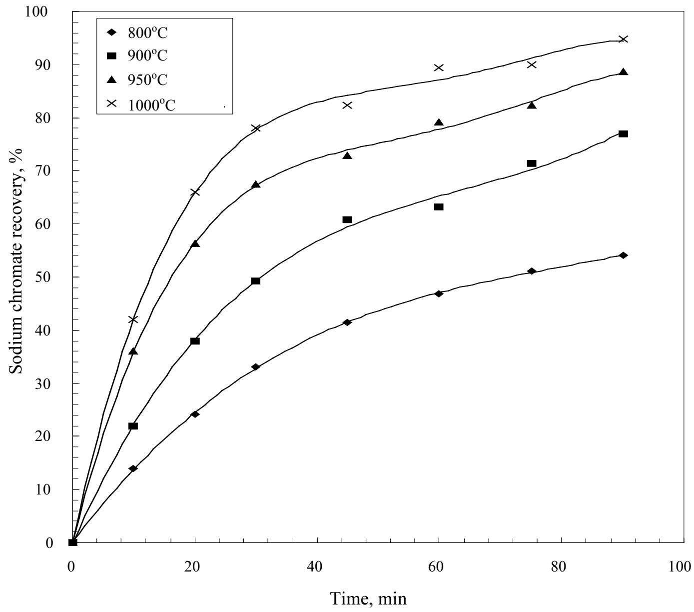

Figure 2. Effect of different temperature on sodium chromate recovery for pellets containing by-pass cement

From Figures 1 and 2, it can be concluded that the addition of by-pass cement leads to increase the sodium chromate recovery at any time and temperature. This may be attributed to the fact that by-pass cement containing free CaO, which is regarded as a catalyst which enhances the rate of formation of sodium chromate (El-Tawil *et al.*, 1991).

3.3. Kinetics of sodium chromate formation

Kinetics of sodium chromate formation from pellets free and containing by-pass cement were studied. Many investigators have studied the kinetics of sodium chromate formation via oxidation of chromite ore with soda ash in the presence and absence of CaO. Various model have been developed in order to represent these kinetics. In this work the solid diffusion models was employed to evaluate the kinetic parameters of the reaction. This model which has also been used by other researcher (Abouzeid, 2002), relates the fractional sodium chromate recovery (R), to the reaction time (t) by the following equation:

$$[1 - (1\text{-}R)^{0.333333}]^2 = kt \qquad (3)$$

This equation provided excellent fits for the experimental data obtained for pellets with and without by-pass cement as shown in Figures 3 and 4.

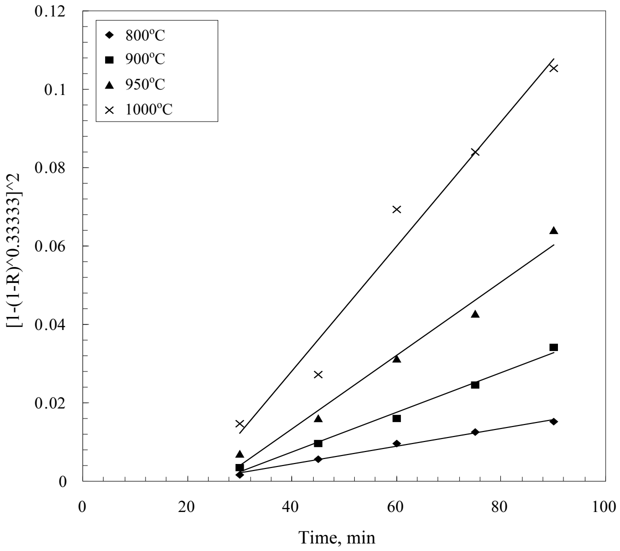

Figure 3. Relationship between solid-state diffusion model ([1-(1-R)^0.33333]^2) and time of reaction for pellet free from by-pass cement and fired at different temperature

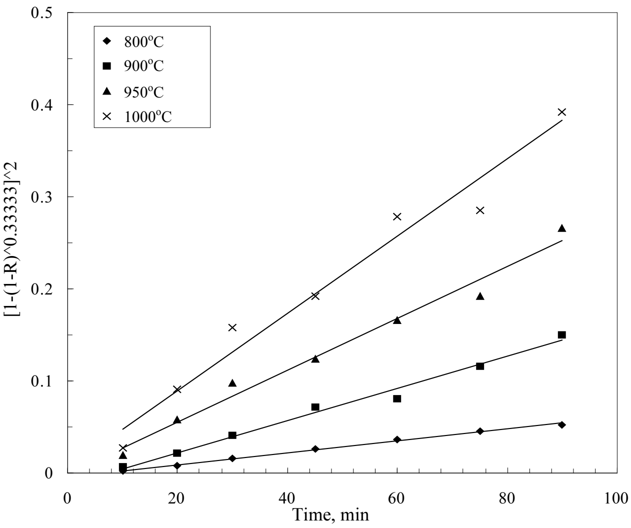

Figure 4. Relationship between solid-state diffusion model ([1-(1-R)^0.33333]^2) and time of reaction for pellet containing by-pass cement and fired at different temperature

The slope of the straight line obtained from the previous fitting represents the rate constant k. The activation energies for the reaction of both pellets, could be calculated from Arrhenius equation:

$k = k_o e^{-E/R`T}$ (4)

Where k is the rate constant, k_o is the frequency factor, E is the activation energy, T is absolute temperature, R` is the universal gas constant.

This equation can take the following form:

$\ln k = \ln k_o - E/R`T$ (5)

Then the slope of the straight line obtained from plotting the relation between Lnk and the reciprocal of the absolute temperature, gives the activation energies of both reactions. Figures 5 and 6, shows the relationship between Lnk and the reciprocal of absolute temperature for both pellets. The activation energy of cement free pellets was 119Kj/mole, while in the presence of cement it was 102Kj/mole. From this result it is evident that the addition of cement dust has a catalytic effect in the production of sodium chromate.

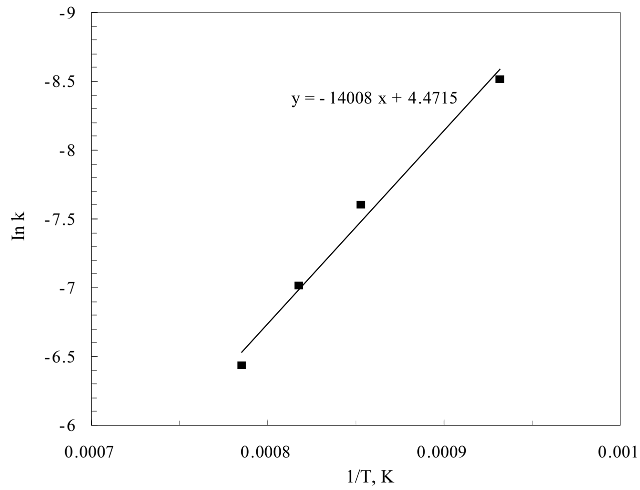

Figure 5. Arrhenius plot for pellets free from by-pass cement and roasted at different temperature

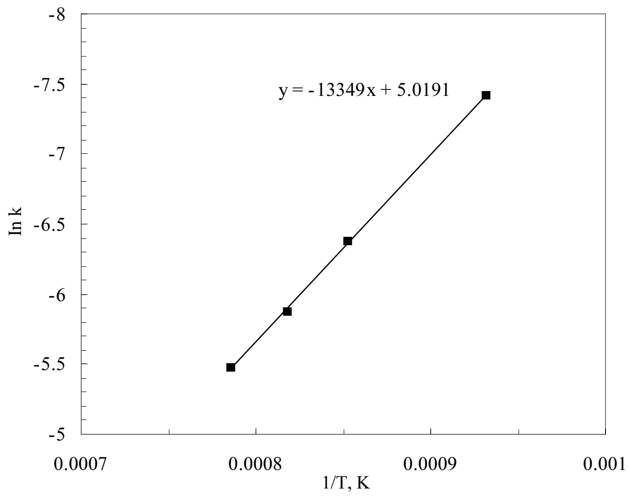

Figure 6. Arrhenius plot for pellets containing by-pass cement and roasted at different temperature

3.4. XRD of the roasted pellets

The x-ray diffractograms of both types of pellets fired at 1000°C for 90min are shown in Figure 10. The main constituents of the pellets free of cement are: Na_2CrO_4, $Na_2CrO_4.4H_2O$, $NaAlSi_3O_8$, Na_2FeO_4 and Na_2SiO_3. These compounds are formed according to the following equations:

$$4Na_2CO_3 + 2Cr_2O_3 + 3O_2 = 4Na_2CrO_4 + 4CO_2 \quad (6)$$

$$Na_2CO_3 + Al_2O_3 + 6SiO_2 = 2NaAlSi_3O_8 + CO_2 \quad (7)$$

$$4Na_2CO_3 + 2Fe_2O_3 + 3O_2 = 4Na_2FeO_4 + 4CO_2 \quad (8)$$

$$Na_2CO_3 + SiO_2 = 2Na_2SiO_3 + CO_2 \quad (9)$$

In case of pellets containing cement, the main constituents are: Na_2CrO_4, Na_4CrO_4, $4CaO.Al_2O_3.Fe_2O_3$, $2CaO.Al_2O_3.SiO_2$ and ß-Ca_2SiO_4. These different constituents may be formed as a result of the following reactions:

$$Cr_2O_3 + 4Na_2CO_3 + 0.5O_2 = 2Na_4CrO_4 + 4CO_2 \quad (10)$$

$$4Na_2CO_3 + 2Cr_2O_3 + 3O_2 = 4Na_2CrO_4 + 4CO_2 \quad (11)$$

$$4CaO + Al_2O_3 + Fe_2O_3 = 4CaO.Al_2O_3.Fe_2O_3 \quad (12)$$

$$2CaO + Al_2O_3 + SiO_2 = 2CaO.Al_2O_3.SiO_4 \quad (13)$$

$$2CaO + SiO_2 = Ca_2SiO_4 \quad (14)$$

4. CONCLUSIONS

From this study, the following conclusions can be arrived at:

1- The optimum amount of water changes with the type of feed materials used. It was 31% for cement free charge, and 33% for charge containing cement. These values gave optimum mechanical properties of both types of pellets.
2- The best disc slopes, which gave optimum mechanical properties of green cement free pellets, was 55°, and 60° for pellets containing cement.
3- The highest residence time of material in the disc, which gave maximum mechanical properties of both types of green pellets, was 10min.
4- By-pass cement proved to act as a catalyst in the way of sodium chromate recovery from the point of view that sodium chromate recovery from pellets containing by-pass cement addition is much higher than that without by-pass cement addition roasted at the same roasting conditions.
5- The energy of activation of pellets without by-pass cement addition was about 119kj/mole. Whereas in case of pellets containing by-pass cement addition it was 102kj/mole. This also proves that by-pass cement addition acts as a catalyst for the sodium chromate recovery from pellets containing chromite ore concentrate and soda ash.

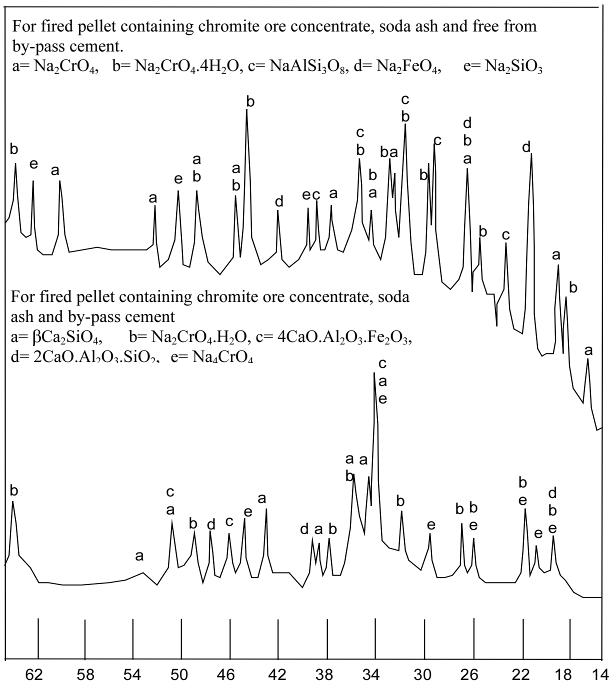

Figure 7. X-ray diffractogram of pellets free and containing by-pass cement after firing at 1000°C for 90min

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