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EFFECT OF SOME ALKALI ADDITIVES ON THE REDUCIBILITY OF AL-HUSSAINIYAT IRON ORE, FROM IRAQI WESTERN DESERT

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ABSTRACT

The reducibility of Al-Hussainiyat pisolitic iron ore with coke and some alkali carbonate additives was investigated. The variable parameters studied are: temperature, time and type and amounts of alkali additives. Initially a precalcined ore of particle size range (–850 +177) micron mixed with coke (–75) micron was reduced in the temperature range (850 – 1000)° C at variable time (60 – 150) minutes. The effect of alkali carbonates (Na_2CO_3, K_2CO_3 and $CaCO_3$) on reducibility was next studied at the same temperature conditions above for (150) minutes. Reduction time and the amount of additive in the coke ore mixture was varied (1 – 5) % of the ore weight.

The experimental results show that, reduction temperature, reduction time and additive amount substantially influence the reducibility and higher degree of reduction was accordingly yielded. The best results were obtained at 5% additive at 1000°C .The effect of additives was found in the following order: $CaCO_3 > K_2CO_3 > Na_2CO_3$.

تأثير بعض المضافات القلوية على القابلية الاختزالية لخام حديد الحسينيات من الصحراء الغربية العراقية

عبد الوهاب عبد الرزاق العجيل و سحر نجم عبد الله

المستخلص

يتناول البحث القابلية الاختزالية لخام حديد الحسينيات ألحمصي مع فحم الكوك وبعض الإضافات من الكاربونات القلوية. العوامل المتغيرة التي تم دراستها هي درجة الحرارة، الزمن ونوع وكمية القلويات المضافة. ابتدءا تم اختزال خليط من الخام المكلسن مسبقاً ذو مدى حجمي (–850 +177) مايكرون مع الفحم (–75) مايكرون وفي مدى الحرارة (850– 1000)° م وبأزمان مختلفة تراوحت بين (60 – 150) دقيقة، تلاها دراسة تأثير الكاربونات القلوية (Na_2CO_3، K_2CO_3 و $CaCO_3$) على القابلية الاختزالية تحت نفس ظروف درجات الحرارة أعلاه، وعند زمن (150) دقيقة حيث تم استخدام كميات مختلفة (1 – 5) % من وزن الخام من المواد المضافة الى مزيج الخام والفحم.

نتائج التجارب بينت بان درجة حرارة الاختزال ، الزمن وكمية المواد المضافة توثر بشكل فعال على القابلية الاختزالية والتي على أساسها تم الحصول على درجة اختزال عالية وان أعلى النتائج التي تم التوصل إليها هي باستخدام 5% وزناً من المواد المضافة عند درجة حرارة 1000°م ولقد وجد إن تأثير المواد المضافة هو وفق التسلسل التالي .($CaCO_3 > K_2CO_3 > Na_2CO_3$)

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INTRODUCTION

Al-Hussainiyate iron ore that is located in the western desert of Iraq is of a low grade sedimentary oolitic – pisolitic type of marine origin (Soframines, 1975 and Mahdi *et al.*, 1993). The bulk of the iron content (averaging 26% Fe_T) of the ore is the form of hydrated iron oxide (goethite – limonite) associated with hematite. These iron minerals are very finally disseminated and intimately associated with impurities of submicron size clay-type mineral (Klockner, 1989 and Al-Ajeel and Mahdi, 2006).

Comprehensives work have been performed to upgrade the iron content of the ore by physical methods, with major emphasize on magnetizing roasting (or reduction roasting) technique. All efforts however were failed to produce concentrate more than 50% Fe_T (Ghanim, 1978; Moslim, 1984; Saud and Naser, 1985; Klockner, 1989 and Ganim, 1996). The magnetizing roasting process is based essentially on reduction of an iron ore oxide with a reducing agent (coke, coal, H_2, CO or a mixture of both gases) at high temperature to produce iron phase (mostly magnetite) possess high Magnetic susceptibility. That can be separated from the ore impurities by low intensity magnetic separation. However, recent work (Al-Ajeel and Mahdi, 2006) suggested segregation roasting alternative as alternative extraction process for the ore. The process involves roasting the ore with chloridizing agent (e.g. $CaCl_2$) in the presence of carbon (coal or coke). In this work, it is claimed that a magnetic concentrate assaying 86% Fe_T was achieved. The formation of HCl gas during heating could be a criticizing factor for this method.

Nevertheless the problem poised by the complex nature of the ore and lack of information of its reducibility (the case at which oxygen can be removed from the iron oxide during reduction) were encourage this investigation. It have been reported that the chemical composition and physical properties of the ore, the temperature and time of reduction besides some additives all of which can affect the reducibility of iron oxides (Stephenson and Smailer, 1980; Bryk and Lui, 2004; Lee *et al.*, 1997 and Lu and Huang, 2003).

The reduction of iron oxide by solid carbon over all reduction is governed by the availability of reducing gas (CO) which produce by gasification of carbon in accordance with the reduction ($CO_2 + C = 2CO$) which is commonly known as the Boundouard reaction (Biswas, 1981). The Boundouard reaction equilibrium as well as the iron oxides phases in equilibrium with different CO gas concentration at variable temperatures is shown in Fig. (1).

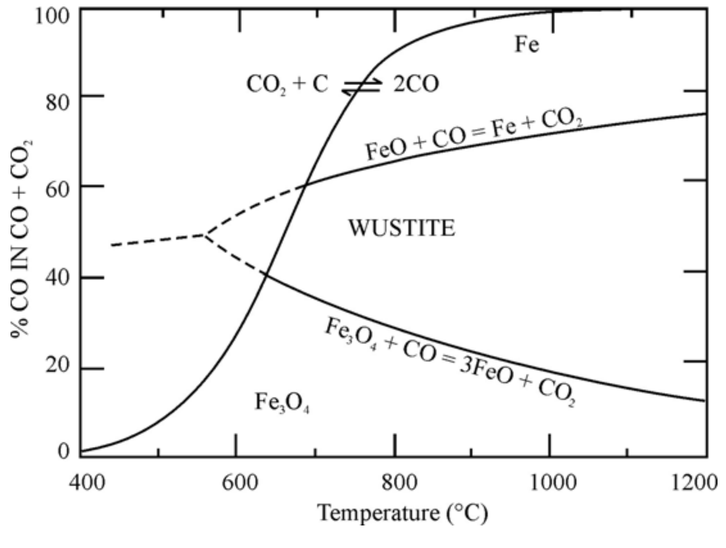

Fig.1: Equilibrium gas composition versus temperature diagram for the iron – carbon – oxygen system

Rao and Han (1984) reported that the rate of the carbothermic reduction of iron oxides is markedly improved by the addition of alkali oxides catalysts. The catalyst promotes the gasification reaction and ensures adequate supply of reducing gas, which in turn enhances the rate of reduction.

The objective of this work is to investigate the reducibility (in term of degree of reduction) of Al-Hussainiyat iron ore by reduction with coke and follow it up with the determination of the effect of three different additives, namely Na_2CO_3, K_2CO_3 and $CaCO_3$. Results were expected to provide insight on the reduction behavior of Al-Hussainiyat iron ore, which accordingly can be utilize in magnetizing roasting technique. The study covered the time and temperature of reduction as well as the amount of additives.

MATERIALS AND METHODS

Pretreated (crushing, screening, and washing) sample of Al-Hussainiyat iron ore received from the R and D department of the State Company of Geological Survey and Mining was used in this work. The results of chemical and XRD analysis are shown in Table (1) and Fig. (2), respectively.

Table 1: Chemical composition of the pretreated iron ore sample

Constituent	Weight (%)
Fe_2O_3	41.49
SiO_2	28.76
Al_2O_3	16.52
CaO	1.68
MgO	0.31
TiO_2	0.93
L.O.I	8.66
Others	1.65

Anhydrous alkali carbonate in a powder form of sodium, potassium and calcium of reagent grade were used as additives. These materials have a minimum purity of about 99.5%.

Foundry coke received from the foundry department of the Technology Institute of Baghdad was used in the reduction experiments. The coke was ground to pass 75 micron sieve opening. Its chemical analyses (ASTM D 271) are shown in Table (2).

Table 2: Proximate analysis of foundry Coke

Constituent	Weight (%)
Fixed Carbon	85.51
Ash	9.74
Volatile matter	4.4
Moisture	0.35

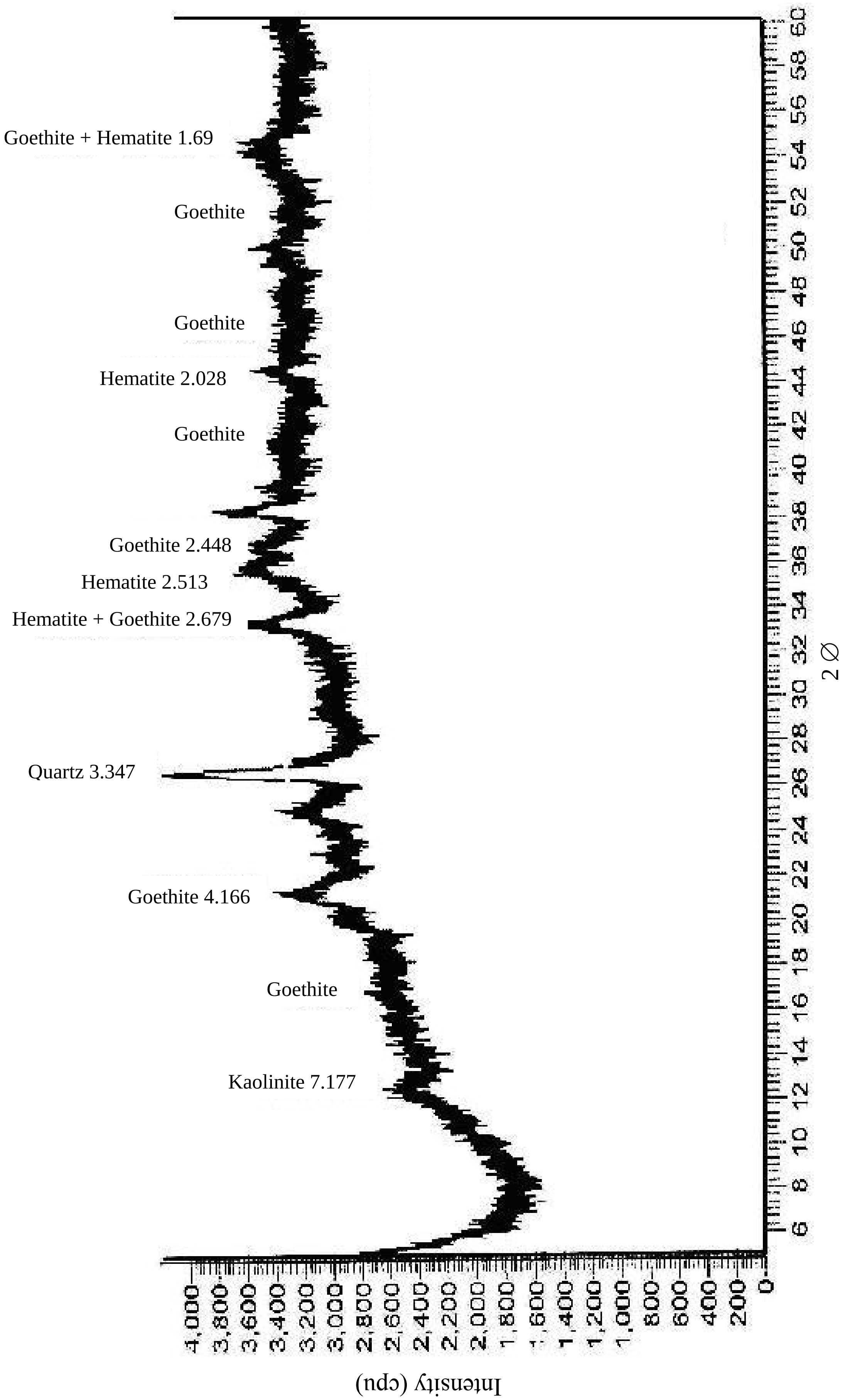

Fig.2: X-ray pattern of Al-Hussainiyat pretreated iron ore

The received ore was treated with combined crushing and screening to have material have a particle size in the range of –0.85 +0.177 mm. For the purpose of this investigation and based on the information gained from the test results of the effect of temperature on weight loss of the ore which show no significant difference between 900°C and 1000°C (Fig.3), the above yielded material was calcined at a temperature of about 900°C prior to any reduction test. This measure was taken to eliminate volatile materials and to essentially to get a constant sample weight. Also to convert the hydrated iron oxide to the more reducible hematite phase Fe_2O_3. Table (3) shows the chemical composition of the calcined iron ore material which is used in all reduction test. For non-additive reduction, 10 g sample of the prepared ore was mixed with 5 g coke (–75 micron particle size). For additive test the amount of ore-coke was mixed in a porcelain dish with various amount of additive, (1 – 5) % by weight of the ore sample and then introduced into a muffle furnace.

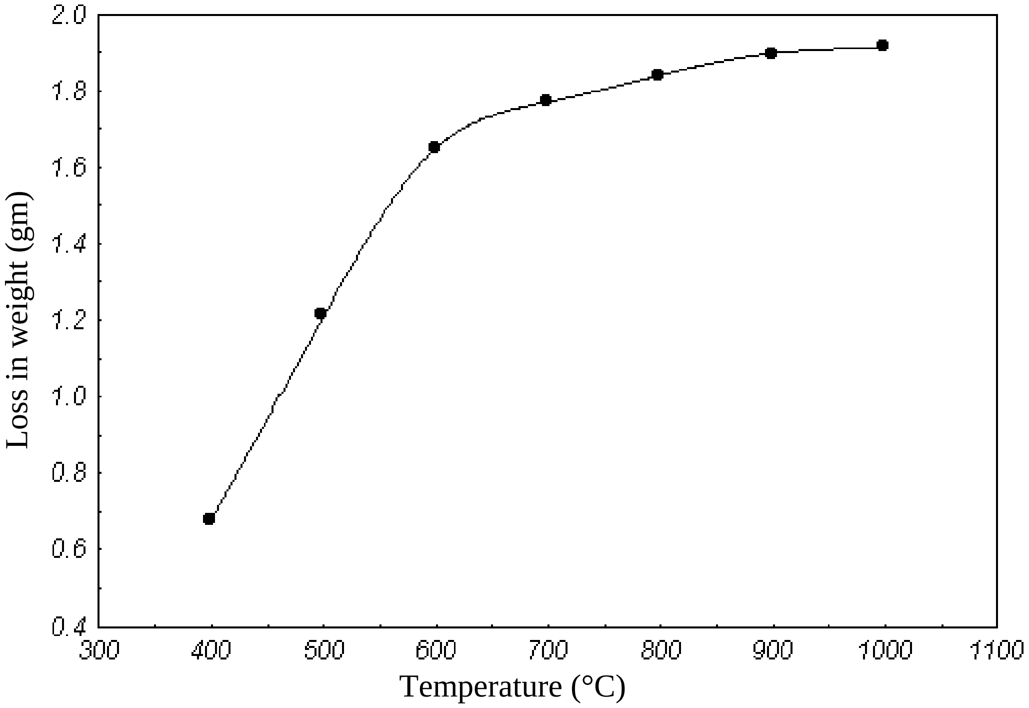

Fig.3: The relation between the losses in weight with temperature

Table 3: Chemical analysis of the heat treated iron ore sample at 900°C

Constituent	**Weight (%)**
Fe_2O_3	48.49
SiO_2	34.26
Al_2O_3	14.63
L.O.I	0.26
Others	2.36

Experiments were conducted with non-additive samples at four different temperatures in the range of (850 – 1000) °C. The reduction time was also varied from (60 – 150) min, while experiments with additive samples were carried out at the same temperature range for a predetermined reduction time. At the end of each test, the mixture was allowed to cool down in the furnace. The reduced material was then sifted on 0.100 mm BS sieve opening to remove the ash, unburned coke, decomposed and undecomposed additive materials. The reduced iron sample was then weighted and the degree of reduction (D.R%) was determined from the following formula (Lu *and Huang*, 2003 and Sterneland *et al*., 2003) :

$$D.R\% = \frac{W_o - Wr}{O_o} \text{ X } 100$$

W_o = weight of ore sample before reduction
W_r = weight of ore sample after reduction
O_o = weight of oxygen of the ore sample before reduction.

RESULTS AND DISCUSSION

The results of the effect of reduction temperature and time on Al-Hussainiyat iron ore (precalcined) with non-additive samples are presented in the form of degree of reduction (D.R%) versus (v) time (t) plot (Fig.4). The effect of additives on reduction was studied under the same temperatures conditions as for non-additive reduction system, at a deduce reduction time. The results of these experiments were presented in the form of D.R% (v) amount of additive plots Figs. (5, 6, 7 and 8) respectively. Histogram plot of D.R% (v) additive type for optimum results was also constructed Fig. (10).

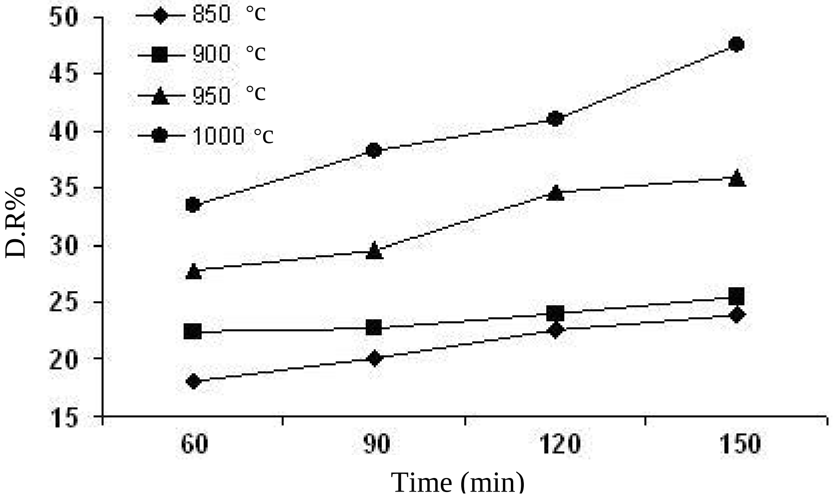

Fig.4: Effect of time on degree of reduction at various temperatures

▪ Effect of Combined Temperature and Time

This series of experiments were principally conducted in order to gain information about the reducibility of the ore before addition of any additive material. It can be seen from Fig. (4), that despite of the profound effect of both reduction time and temperature, the reducibility of the ore is very low. The results indicated that, even after 150 min reduction time, at 1000°C, only about 48% D.R was achieved. This can be most likely attributed to the fact that, in acid ore, silica hindered the reduction of iron oxide by forming fayalite (ferrous silicate), which can form from magnetite, wustite (FeO) and even directly from hematite (Biswas, 1983 and Stephenson and Smailer, 1980). Fayalite is well known to have high resistance to reduction and tend to form a glassy phase at high temperatures that seals of the pore (the porosity of the ore was obviously enhanced during the precalcination step due to the release of water of hydration), and hindered the reducing gas diffusion However, the low degree of reduction coupled with poor liberation of iron oxide due to the complex nature of the ore could be the behind of difficulties the achievement of high iron magnetic concentrate, by conventional reduction roasting operation. The data out lined by the workers Geomin (1978); Moslem (1984); Saud and Naser (1985); Klokner (1989) and Ghanim (1996) were very good evidence of the problem. However, because the whole reduction process take place in the solid state, the increase in the reducibility of the ore is strongly essential.

- **Effect of Additives**

The effect of different amount of additives (Na_2CO_3, K_2CO_3 and $CaCO_3$) on the reducibility of Al-Hussainiyat iron ore at different temperatures (850, 900, 950 and 1000) °C for 150 min, as reduction time are shown in Figs. (5, 6, 7 and 8) respectively. It can be observed from. These figures, that the additives have a marked effect on the reducibility of the ore. It is also seen that the effect is directly proportional to the amount of the additives. The higher D.R% was achieved (within the range of the additives amounts used in this work) was at amount of 5 wt%. A comparison of the results (Figs.5, 6, 7 and 8) shows that the degree of reduction is significantly increased as the temperature increases. For clarity, the data presented in these figures were reproduced and presented in Fig. (9), from which it can be seen that the reducibility exhibit excellent results as the temperature rise to1000°C, particularly for K_2CO_3 and $CaCO_3$. Figure (10) shows clearly the effect of the three types of additives on the degree of reduction, and hence on the reducibility of Al-Hussainiyat irons ore. The effect of the additives can accordingly be rank as follow: $CaCO_3 > K_2CO_3 > Na_2CO_3$. it is worth to point out here that these results are generally agreed with that reported in the literatures (Rao and Han, 1984 and Mookherjee, 1986) that the rate of carbothermic reduction of iron oxides were markedly enhanced by the addition of alkali carbonate, in the order, $K_2CO_3 > Na_2CO_3 > Li_2CO_3$.

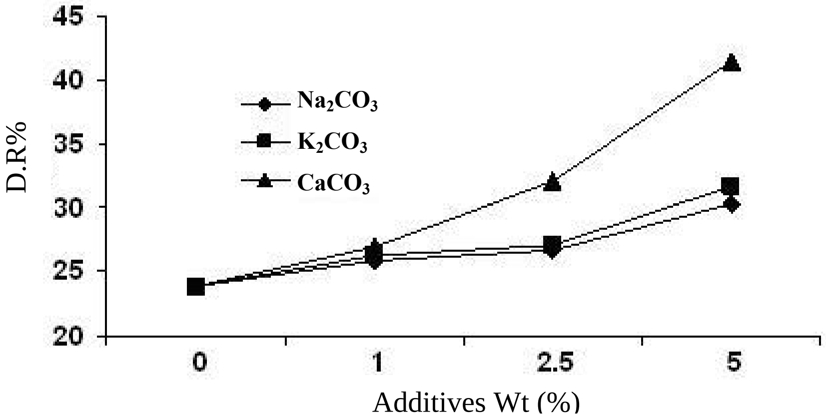

Fig.5: Effect of amount of additives on degree of reduction at 850°C for 150 min

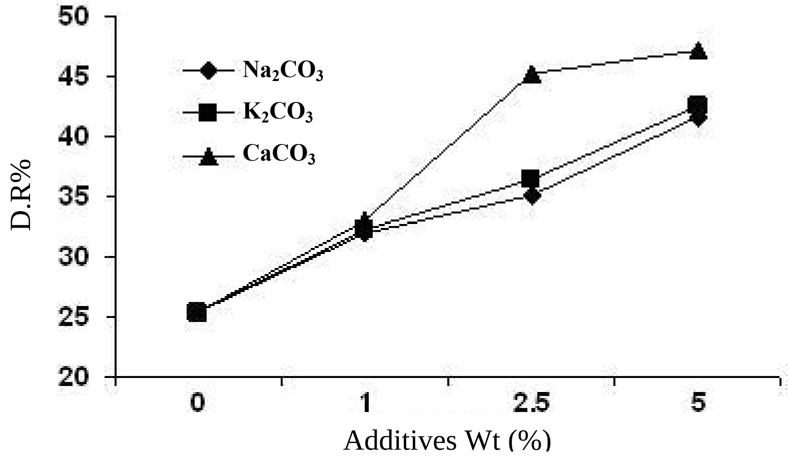

Fig.6: Effect of amount of additives on degree of reduction at 900°C for 150 min

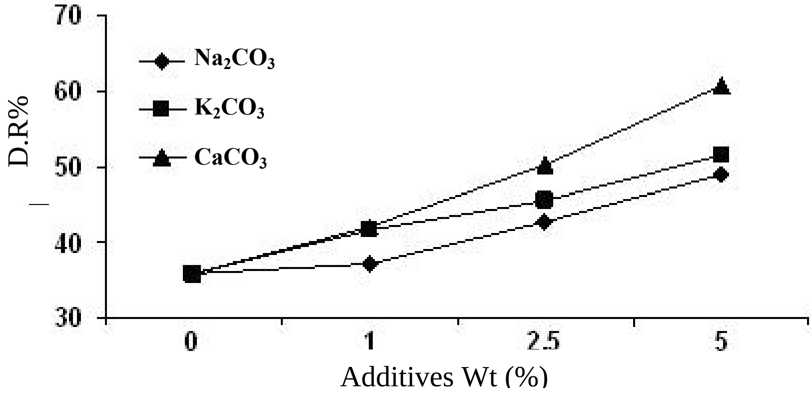

Fig.7: Effect of amount of additives on degree of reduction at 950°C for 150 min

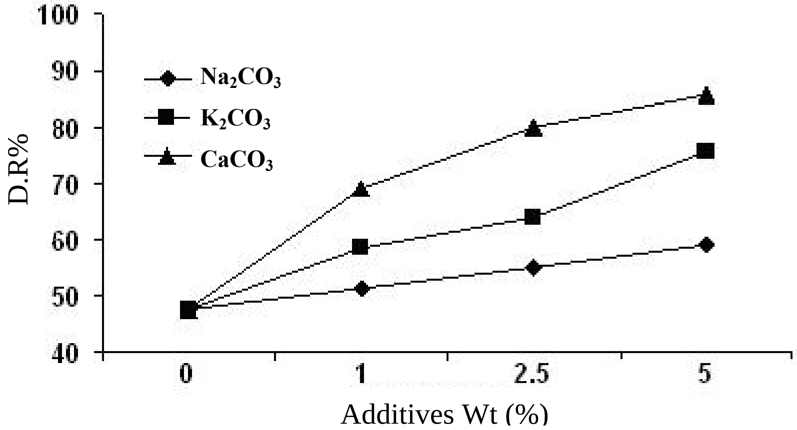

Fig.8: Effect of amount of additives on degree of reduction at 1000°C for 150 min

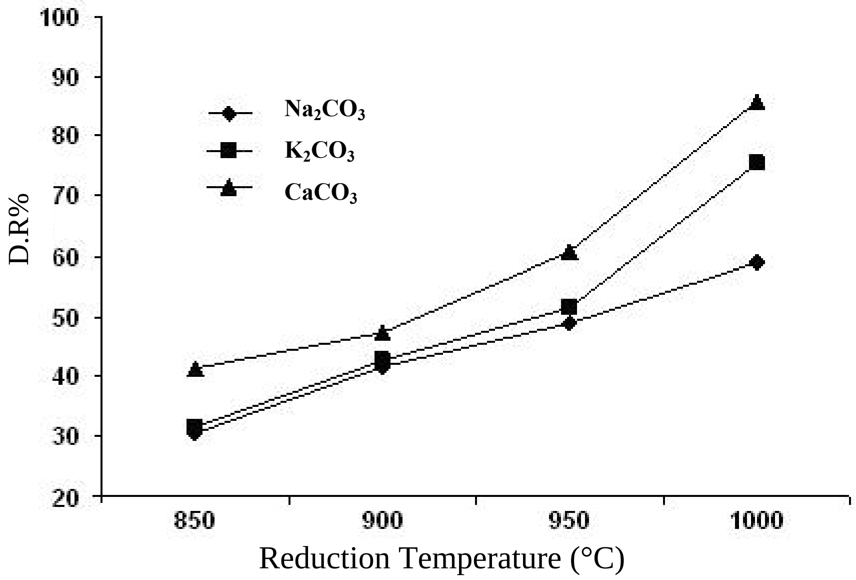

Fig.9: Effect of reduction temperature and additives type at 5% additive on degree of reduction

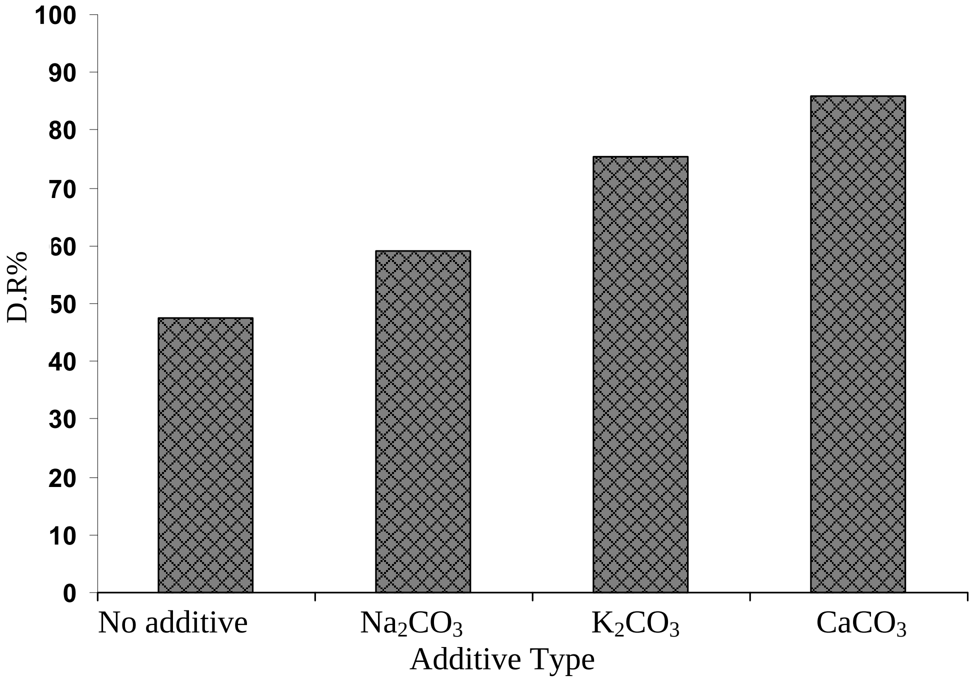

Fig.10: Effect of different type of additives on degree of reduction at 1000°C/ 150 min reduction time and 5% additives

X-ray (XRD) examination of reduced samples at 1000°C with 5 wt.% additive of K_2CO_3 and $CaCO_3$, confirm that these alkali carbonates are incorporates in the lattice of iron oxide as shown in Figs. (11 and 12). Therefore, it can be deduce that the alkalis create catalytic reaction conditions, which reflect the noticeable changes in the degree of reduction behavior.

A great important action of the catalytic effect is most probably attached on the gasification reaction of carbon ($C + CO_2 = 2CO$). It has been reported by Biswas (1981); Rao and Han (1984); Matsunami *et al*. (1999); Shinya *et al*. (1999) and Zahou *et al*. (2007) that some metal carbonate, like Na_2CO_3, K_2CO_3, $CaCO_3$, Li_2CO_3 and $CaCO_3$. $MgCO_3$ (dolomite) exert a positive catalytical effect on the carbon gasification reaction. These literatures also show that the mechanism of alkali gasification is not well understood and were of a great deal of controversy and not the same for all catalysts. However, it is generally agreed that the carbon gasification is largely accelerated in the present of alkali carbonate, compared to non-alkali system. An average of three – four fold increase in the rate of reduction has been generally recorded in the aforementioned publications.

It can be anticipated that the catalytic effect on the gasification reaction, results in higher CO generation that lead to more iron oxide reduction and hence yielded higher degree of reduction. Obviously, the CO_2 source for the gasification is generated from the decomposition of the carbonate additive, as well as from the reduction of iron oxide by CO (e.g. $3Fe_2O_3 + CO = 2Fe_3O_4 + CO_2$). Accordingly, the reduction and gasification reactions are thus necessarily coupled. At the meantime, it is worth to mention that carbon gasification with CO_2 to produce CO occurs at temperature above 800°C (Biswas, 1981 and Lu *and Hung*, 2003).

For reduction without additives (Catalysts) the initial CO required for the reduction could be made available through direct reduction of carbon with iron oxide and also from that released from the oxidation of carbon during heating. The CO_2 needed for the gasification reaction is, then produced by the reaction of CO with iron oxide. Henceforth, the reduction of iron oxide is much lower than that with additive system due to low CO generation which in turn yields lower degree of reduction.

However, it should be point out that other effect of the alkali carbonate may be possible during the reduction process. It has been recorded (Biswas, 1981; Elkasabgy, 1984 and Basulmallick, 1995) that the presence of alkalis enhances cracking and swelling of iron ore, pellets and sinters. Therefore, it is expected that the mass transfer of reducing gas between the iron oxide grains will be enhanced and hence higher reduction occur. Accordingly, it can be stated that Na_2CO_3, K_2CO_3 and $CaCO_3$ exerts a positive effect on the reducibility which reflected by high degree of reduction, and that, the ways of action of the three additives are differ at lower and higher temperatures, as illustrated in Fig. (9).

CONCLUSIONS

From the current work, it can be concluded that:

- The iron oxide, carbon and additive system is a complex one and therefore, there is no general mechanism that can lead to a clear cut method for the interpretation of the obtained data.
- Al-Hussainiyat iron ore, coke reduction additive Na_2CO_3, K_2CO_3 and $CaCO_3$ system have effective influence of the reducibility of the ore.
- The degree of reduction has been found to increase with increasing additive amount and temperature within the selected experimental range and conditions.
- The catalytic effect of $CaCO_3$ is better than both Na_2CO_3 and K_2CO_3, the effect is ranked as follows: $CaCO_3 > K_2CO_3 > Na_2CO_3$

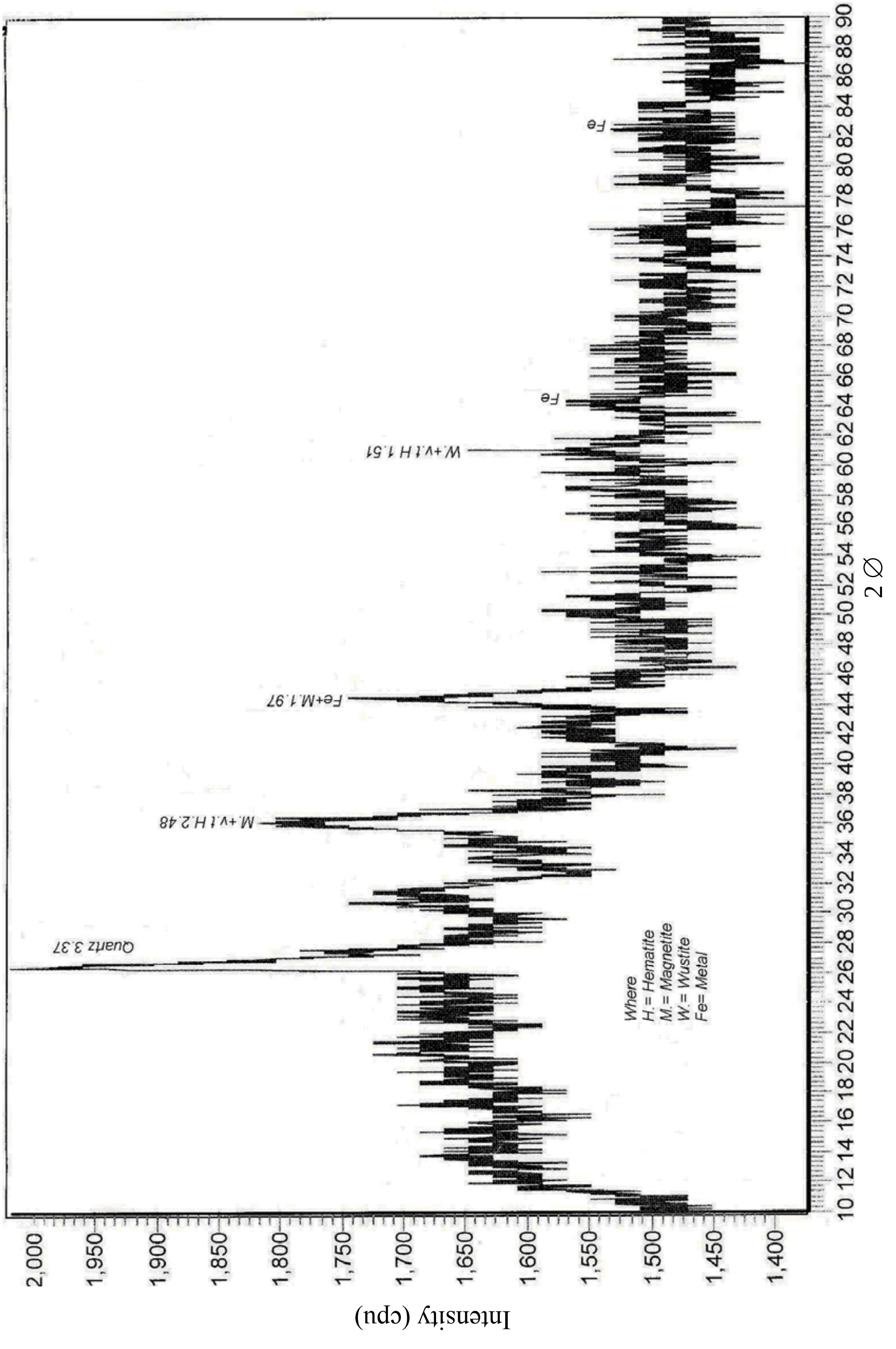

Fig.11: X-ray pattern of reduced iron ore with K_2CO_3 addition

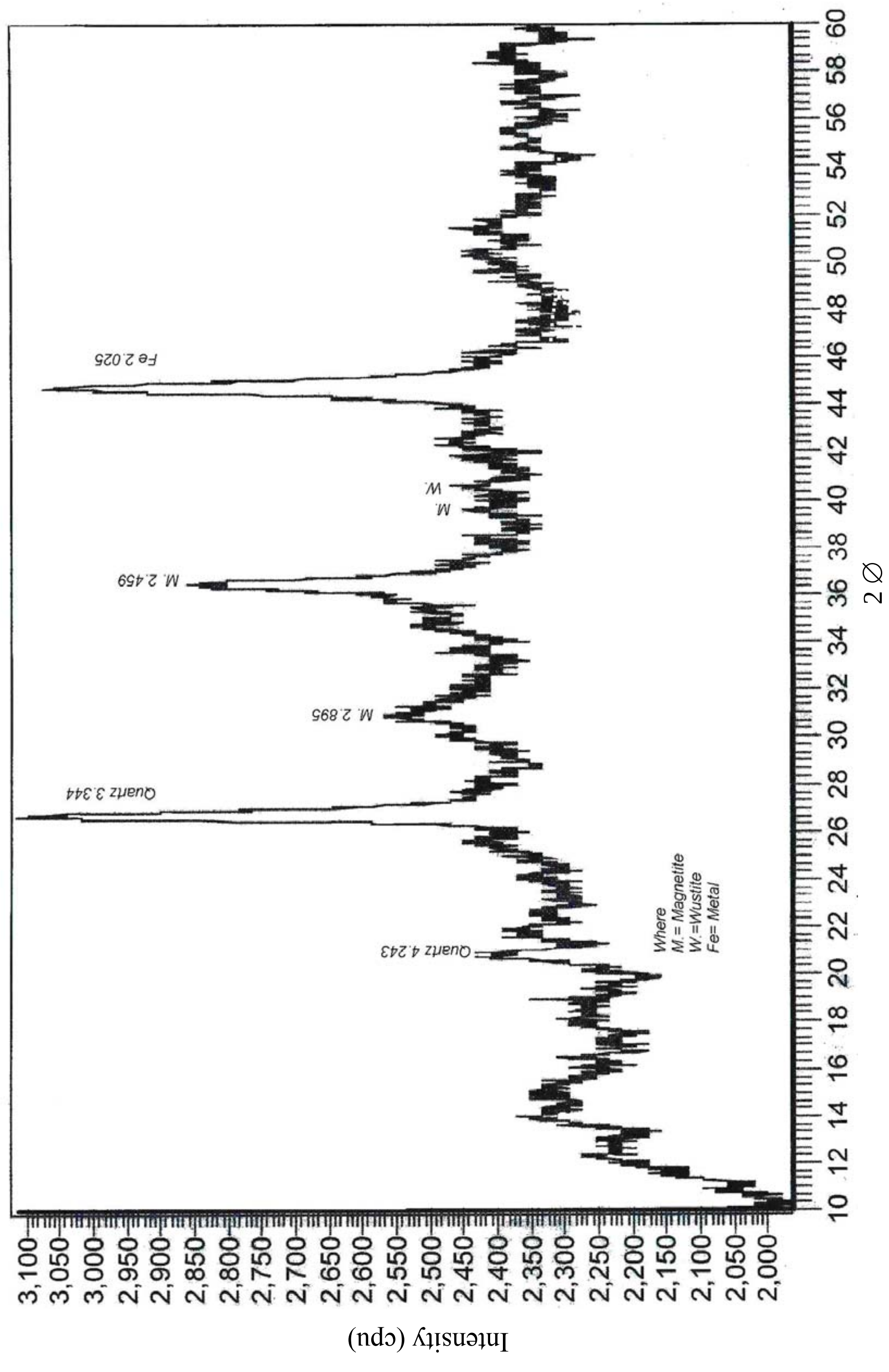

Fig.12: X-ray pattern of reduced iron ore with $CaCO_3$ addition

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