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Study of smelting Egyptian black sand ilmenite by using El Maghara Coal

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Ilmenite smelting, Titania slag, cast iron, carbothermic reaction, black sand

Abstract: Black sand is beach deposits that come from the headwaters of the Nile, which are rich in heavy minerals. The major economic mineral is ilmenite. It represents around 60 – 70 % of economic minerals quantity. To increase the adding value of the national resources, a series of experiments to study the smelting process for producing high Titania slag and cast iron. The effect of many factors such as time (20, 25 & 30 min), carbon content (15 %, 20 % & 30 %) and using a flux (1 %, 2 % & 3 %) were studied. The results revealed that time of the experiment has the most significant affecting on the iron yield among other factors. The maximum obtained iron yield was about 80.5 % and the assay of titanium dioxide in Titania slag was about 77.6 % for 30% carbon at 30 minutes.

1. **Introduction**

The Egyptian black sand is considered one of the important resources that contains strategic and economic heavy minerals that are required for industrial exploitation whether for the nuclear industry or other metallurgical and engineering industries [1-3]. Large-scale placer deposits of black sands are dispersed throughout the Nile Delta's northern Mediterranean coastal plain as well as the Sinai Peninsula, specifically in the coastal length between Abu Qir Town in the west and Rafah City in the east of the Egyptian frontiers. There is a chosen area which evaluated to obtain the economic beach mineral contents to the east of Rosetta. It has an acceptable probable reserve in an area of 13 km2 and 10 meters depth. The obtained explored reserve was about 146 million tons of raw sand with average total economic minerals content ranging between 0.83-1.12 percent distributed as follows [1]:
Magnetite = 0.48 – 0.56%, ilmenite = 0.50 – 0.78%, rutile = 0.02 -0.07%, zircon = 0.04 -0.13%, monazite = 0.003 -0.004%.

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These sediments contain strategic and economic heavy minerals that are required for industrial exploitation whether for the nuclear industry or other metallurgical and engineering industries. Titanium dioxide for the nuclear industry and paints could be produced from the rutile concentrate. In the meantime, zircon as a mineral would be used in the ceramic industry whereas rutile as a mineral would be used in the welding rods industry [1, 4]. The production of ilmenite was carried out according to the proposed flowsheet as shown in Figure (1). In the first upgrading of the economic minerals by gravity process (spirals) then separate ilmenite by using low-intensity magnetic separator. To improve the ilmenite quality, we use a shaking table.

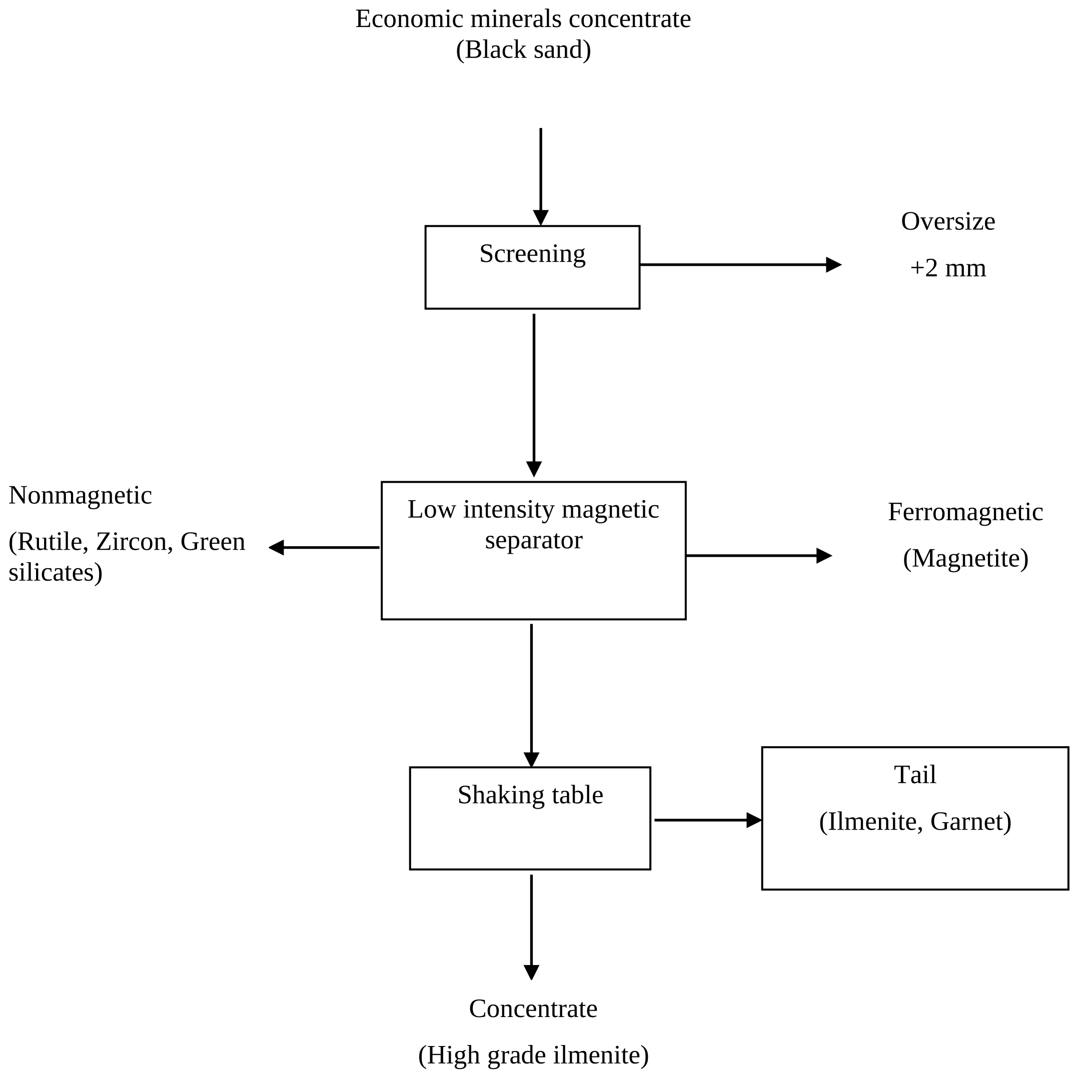

Fig. 1: the flowsheet of ilmenite production

The purpose of ilmenite smelting is to upgrade ilmenite to a suitable feedstock for sulfate and chloride pigment producers. The important role of ilmenite smelting is illustrated by the volumes of feedstock that it provides pigment producers. In 1994, high-–titania slag represented just over 50% of the mass of feedstock provided to pigment producers [5]. The importance of ilmenite smelting in the Ti / TiO_2 industry can therefore not be ignored. It also appears likely that this route of upgrading minerals to suitable feedstock for the pigment industry will grow relative to synthetic rutile production due to the impact that the waste materials produced from synthetic rutile processes have some negative effects on the environment. There are eight companies in the world, other than Russia, engaged in the recovery of Titania from ilmenite by the slag route shown in Table (1)

Table 1: Metallurgical process options for beneficiation of ilmenite to titania slag [5]

Process	Description	Plant status
QIT-Electro smelting	Carbothermic smelting of hard rock ilmenite at 1700oC to pig iron and sulfate titania slag (86-87%)	SOREL Quebec 1000000 tons per year slag
RTZ Iron & Titanium Electro smelting	Carbothermic smelting of beach sand ilmenite at 1700oC to pig iron and sulfate titania slag (86-87%)	Richards Bay, South Africa, 1000000 tons per year of slag and 500000 tons per year of pig iron
Submerged arc smelting process	Pre-reduction of ilmenite (50% TiO_2), followed by smelting in an arc furnace to produce pig iron and titania slag (87% TiO_2)	TINFOS, Norway, 200000 tons per year of slag and 100000 tons per year of pig iron
Plasma DC arc smelting technology (south Africa Anglo American Corp.)	Carbothermic smelting of ilmenite in DC arc plasma furnace to pig iron and titania slag	NAMAKWA Sands Ltd., South Africa, 1100000 tons per year of slag and 450000 tons per year of pig iron ISCOR, South Africa, 220000 tons per year slag
Cochin Minerals & Rutile Ltd.	Wah-Chang process: reduction roasting, two-stage leaching with 30% HCl, oxidation of first leach liquor to FeC_{l3} for sale. TiO_2 recovery: 88%.	18 000 (95% TiO_2 for export)
Kerala Mineral & Metal Ltd.	Benelite process: reduction roasting, two-stage leaching with regenerated acid	18 000 (89% TiO_2 for in-house use)
Dhrangadra Chemicals Ltd.	20 000 (95% TiO_2 for export Wah-Chang process: reduction roasting, leaching with 30% HCl, disposal of leach liquor, TiO_2 recovery: 90%.	7000 (92% TiO_2 for export)
IREL (OSCOM)	Benelite process: reduction roasting, three-stage leaching with regenerated acid, TiO_2 recovery < 70%	7000 (92% TiO_2 for export)

The main mineral source of titanium dioxide, TiO_2, is ilmenite, $FeTiO_3$. Iron oxides in ilmenite can be metalized by selective reduction, commonly known as pre-reduction, leaving behind TiO_2 and metallic iron. These can be separated by melting. Utilizing carbon monoxide gas produced by partially combusting coal, ilmenite's iron is reduced. To decrease CO_2 emissions, natural gas can substitute coal as a reducing agent. Natural gas, primarily CH_4, can be reformed into so-called synthesis gas, a mixture of carbon monoxide, CO, and hydrogen, H_2 [6, 7]. So, it was suggested using El Maghara coal (bituminous coal) as reductant agent. It contains fixed carbon and the major compound of natural gas, which is methane (CH_4) to gain both effects. This study is considered as a step for using national resources for facing the complicated problems of global supply chains and increasing the adding value of national resources. Also, it enhances the technology of using the national resources.

Authors indicated that the reduction process of ilmenite proceeds through different stages with the formation of intermediate structures between iron and reduced forms of titanium oxides, and the oxygen deficiency in reduced titanium dioxide increased by an increase in reduction temperature and period [8].

Effective separation of iron slag during the electric furnace smelting of titanium slag is a crucial stage. In recent years, various studies have been conducted on the enhanced reduction of ilmenite concentrate by the use of additives [9]. Adding an alkali flux agent (CaO) is for two purposes, the first, is to reduce the melting point of the slag and then decrease the viscosity. The second purpose is to replace iron oxide in the ilmenite matrix, and then push the reduction process. The reaction between added flux and ilmenite is shown in eqn. (1). Such reaction is exothermic in nature according to eqn. (2). For these reasons, white cement was chosen as a fluxing agent. The melting point of calcium titanate is 1970 ^{o}C, but the lowest melting point is 1470 ^{o}C at titanium dioxide around 81.5 %, as shown in Figure (2). On the other hand, the content of silica in the white cement also decreases the melting point of the slag [10, 11].

2. Experimental work

To melt concentrated black sands, a small electric arc furnace (EAF) was assembled, as shown in Figure (3): A DC electric arc furnace was designed and constructed to work with powder and pelletized raw materials. The electric arc furnace should have a powerful transformer, high thermal and electrical efficiency, and a lining made of high-grade refractory (Alumina). The furnace is supplied at 50 Hz using a tapped Spawarka Wirowa ew-23u 300A power transformer with a high current secondary at 200 Ampere, the connection between the transformer and the electrodes is a length of flexible cable which allows the electrode to be moved vertically. Melting is achieved by the heat generated by the electric arc drawn between the electrodes. The feed of EAF is a mixture of 100 gm. of

Ilmenite and different assays of coal. In some experiments a little bit of flux to study the effects of carbon content and time and other factors on the product (cast iron and titania slag).

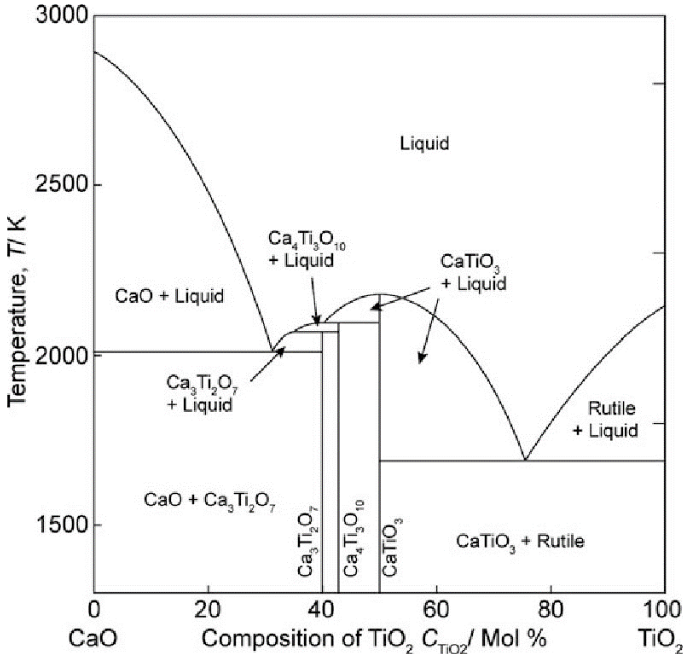

Fig. 2: Equilibrium phase diagram for CaO – TiO_2 binary system [12]

$$CaO + FeTiO_3 = CaTiO_3 + FeO \quad \Delta G^o = -0.1845T + 49.636 \text{ (kJ/mole.K)} \tag{1 [13]}$$

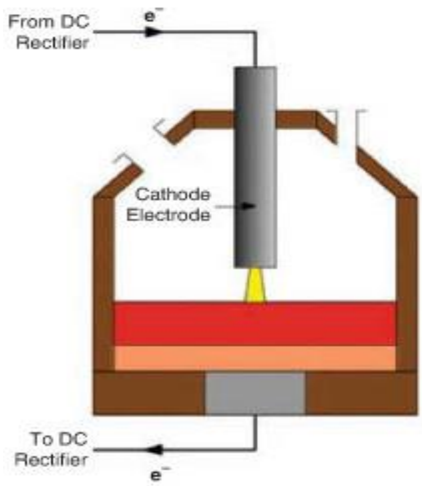

Fig. 3: Schematic for assembled DC electric arc furnace used in experiments.

In this work, national resources from minerals (ilmenite) and reductants (coal) are used. The ilmenite ores are available and located at two main deposits. The first deposit is estimated to be about 50 million tons. It is igneous in nature and is present as lenticular, vein-like, or disseminated bodies intimately associated with metagabbro at several places in the southeastern desert. The chief ore bodies occur in the Hamata region of El-Nasr phosphate company mines at Abu-Ghalaga, which is located 20 kilometers to the west of Abu-Ghusun port on the western of the Red Sea at about 750 kilometers south of Suez. The second ilmenite ore occurs as an essential constituent of beach placers, called black sands. That's the mineral used in this study, and its analysis shown in Table (2). Supermini200 benchtop wavelength dispersive X-ray fluorescence (WDXRF) spectrometer was used to analysis ilmenite, Titania slag and the produced iron.

The used reductant is Maghara coal. The Maghara coal was classified as medium volatile bituminous coal, and its contents are shown in Table (3). The volatile matter obtained during the pyrolysis of coal consists mainly of combustible gases such as hydrogen, carbon monoxide, and methane plus other hydrocarbons, tar vapors, ammonia, and oxygen compounds [14, 15]. So, the volatile matter can replace natural gas as a reductant, which is used in other studies. The main compounds of volatile matter of coal are methane and ethane, which are similar to natural gas [16].

Table 2: Egyptian Beach Ilmenite chemical analysis

Oxides	**Egyptian Beach Ilmenite composition, % wt.**
TiO_2	46.24
FeO	18.63
Fe_2O_3	31.18
SiO_2	0.32
Al_2O_3	0.87
P_2O_5	0.04
MgO	0.64
CaO	0.12
MnO	1.35
Cr_2O_3	0.28
V_2O_5	0.14
S	0.03

Table 3: Maghara coal chemical analysis [17]

Ash	7.54 %
Volatile	52.64 %
Moisture	2.15 %
Fixed carbon	39.82 %

To study the parameters that affecting on ilmenite smelting process such as carbon content, time of experiment, carbon efficiency, flux, and making the inputs as pellets, seventeen experiments were carried out. The overall equation for the carbothermal reduction process is shown in eqn. (2) and (3). Both reactions are favorable above 1200 °C [18].

$$FeTiO_3 + C \rightarrow Fe + TiO_2 + CO_{(g)},$$
$$\Delta G^o = -0.285T + 167.40 \text{ (kJ/mole.K)} \quad (2)$$

$$3FeTiO_3 + CH_{4\,(g)} = 3Fe + 3TiO_2 + CO_{(g)} + 2H_2O_{(g)},$$
$$\Delta G^o = -\,0.673T + 366.64 \text{ (kJ/mole.K)} \quad (3)$$

3. Results and Discussions

The output factor is the iron yield percentage, shown in eqn. (4). According to Table (2) we can calculate the amount of iron in the used ilmenite ore since the atomic mass of iron is 55.847 amu, one mole of iron atoms would weigh 55.847 grams, the atomic mass of oxygen is 16 amu, and one mole of oxygen atoms would weigh 16 grams. So, the weight of iron in the used ilmenite ore is 36.289 gm for each 100 grams of ilmenite. By using eqn. (5)

$$\text{Iron Yield \%} = (\text{Actual Yield / Theoretical Yield}) \times 100 \quad (4)$$

$$Fe = (56/72) \times 18.63 + (112/160) \times 31.18 = 36.289 \text{ gm} \quad (5)$$

In studying the effect of carbon assay on the process of ilmenite smelting, Maghara coal to increase the added value of national resources. The coal is used in different amounts to study the effect of reducing agent amount on the iron yield: 15, 20, and 30%. Per 100 gm of ilmenite. It is clear from Figure (4) that the iron yield is direct proportionally with the Carbon assay. However, in the case of carbon content (30%), the increase is slight and closer to stability compared to the other two cases. This means that time is responsible for increasing iron yield. Effect of time experiments studied at 20, 25, and 30 minutes, at (15, 20, 30) % carbon content. Figure (5) is a study of the effect of time on iron yield at different carbon contents (15, 20, and 30) % of the feed. It is clear from the figure that the increase at 30 minutes is much greater compared to 20 and 25 minutes. It is also clear that the iron yield at 30 minutes, regardless of the carbon content, is very close. This also means that the effect of carbon content on iron yield is not noticeable, and that time has the upper hand.

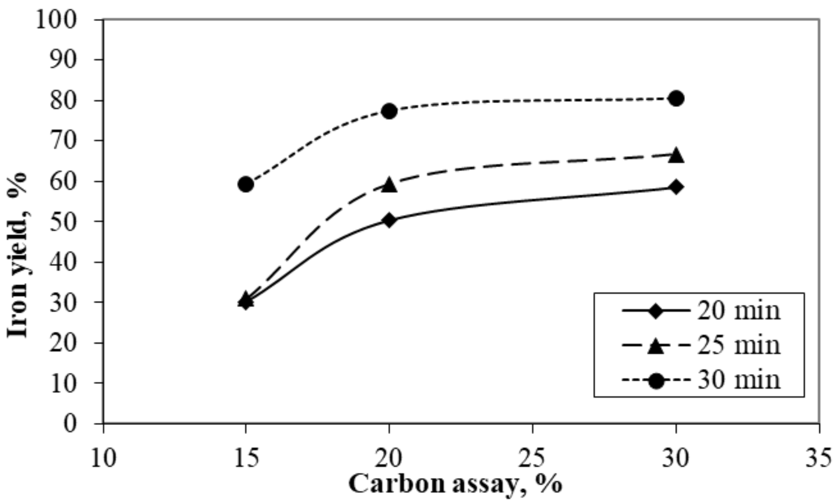

Fig. 4: effect of carbon assay on the iron yield at different times

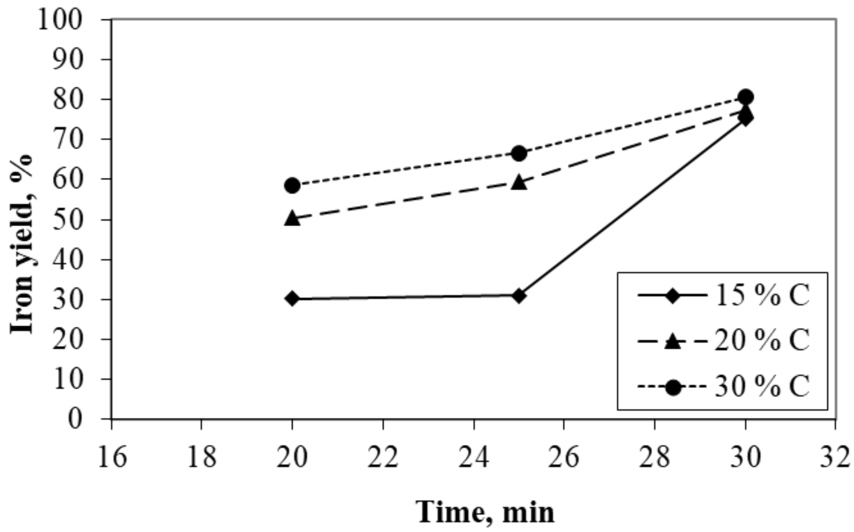

Fig. 5: effect of time on the iron yield at different carbon assays

Carbon efficiency means the ability of carbon to reduce the iron in the feed used. To calculate the amount of iron that should be reduced carbon reduced, we use eqn. (6). At carbon assay 30%, the theoretical iron yield is over 100% of iron content. So, to calculate the carbon efficiency in this assay, the theoretical iron yield equals full iron content.

$$\text{Carbon efficiency} = (\text{iron yield} / \text{theoretical iron yield}) * 100 \qquad (6)$$

Where theoretical iron yield is the calculated iron yield by using eqn. (5) and depends on carbon assay.

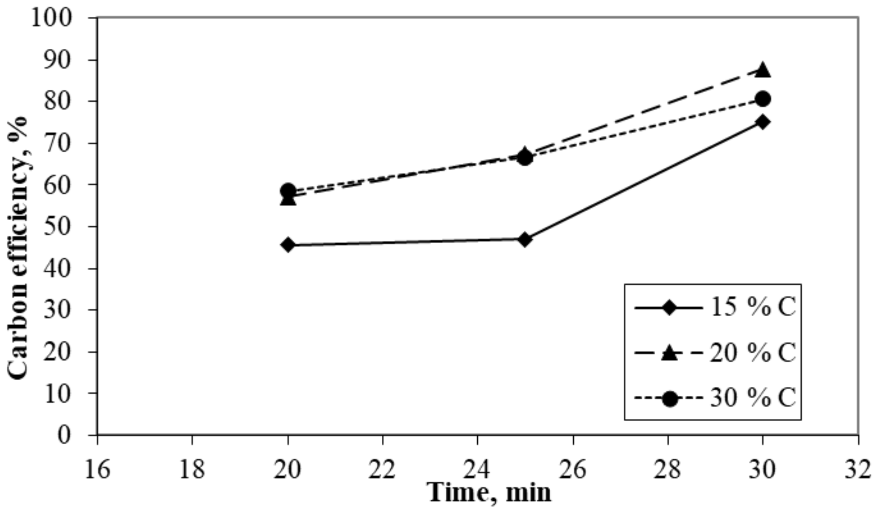

Fig. 6: Effect of time on carbon efficiency at different assays of carbon

The effect of time on the carbon efficiency at different assays of carbon (15, 20 & 30%), is shown in Figure (6). As increasing time, carbon efficiency increases. An efficiency of 20%

is better than efficiency of 30%. By increasing the carbon assay, the iron yield increased, and so titanium oxide increased in the slag. So, the melting point increases, then the viscosity increases. When the viscosity increases, the separation efficiency of iron decreases.

Figure (7) shown, the effect of carbon assay on the carbon efficiency at different times (20, 25 & and 30 min.). By increasing carbon assay, carbon efficiency increases. The carbon efficiency is almost stabilized after a 20% carbon assay. By increasing the time, the iron yield increased. By increasing the time, the furnace temperature increases and so, the viscosity decreases [8, 19]. When the viscosity decreases, the separation efficiency of iron increases, then the carbon efficiency increases.

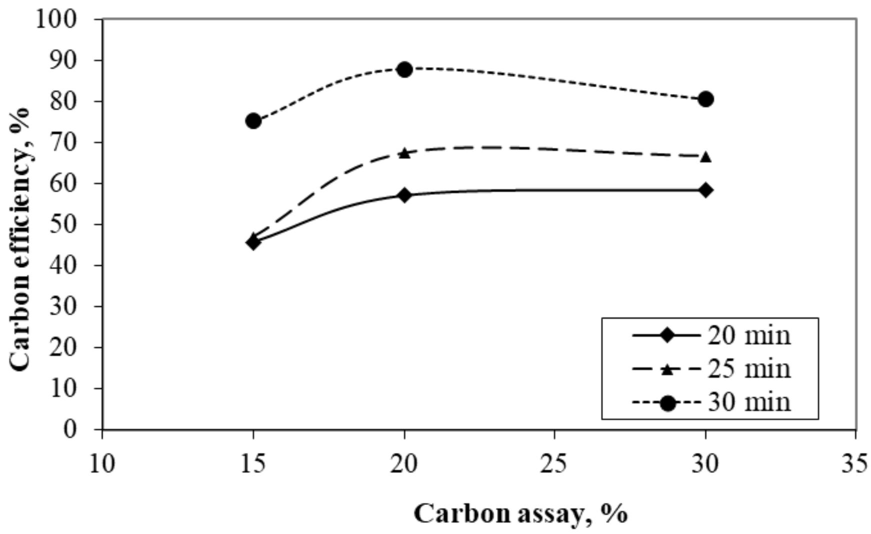

Fig. 7: Effect of carbon assays on carbon efficiency at different times

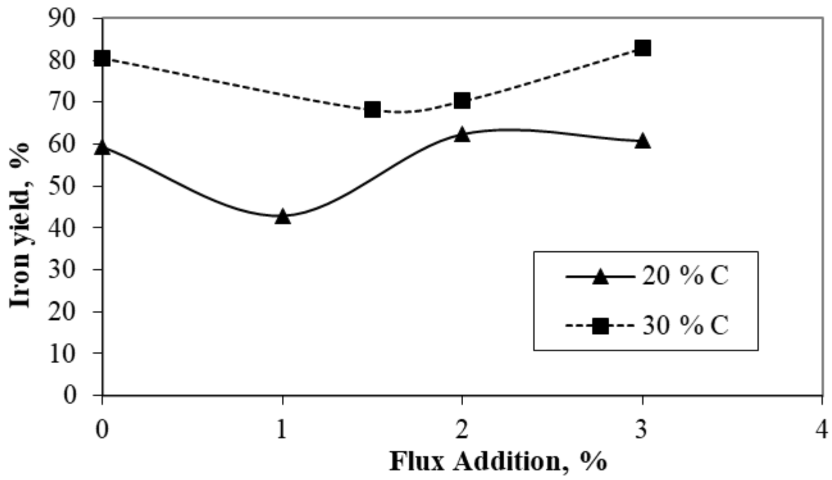

Fig. 8: Effect of flux agent on iron yield

Figure (8) shows the effect of the flux agent on iron yield at different assays of carbon (20 and 30%) for 30 min. At carbon 20%, by increasing flux addition, the iron yield decreases, then returns increasing after 1% flux assay. At 30% carbon assay, the iron yield decreases but returns increase after a 2% flux assay. The returning flux assay at 30% carbon is greater than at 20% carbon assay. The content of titanium dioxide in the slag at 30% carbon assay is greater than at 20% carbon assay. It means that the melting point of the slag which produces at 30% carbon assay is higher than that at 20% carbon assay, and so, the viscosity [20, 21]. When the viscosity increases, the separation efficiency of iron decreases, then the iron yield decreases. The flux reacted according to eqn. (6). In Table (4) shown that, XRF analysis for metal composition for the optimized condition, which are 30% carbon assay at 30 minutes. It appears that the produced metal can be considered as a primary material to produce ductile cast iron. It has a manganese content of less than 0.4%.

Table 4: XRF analysis of metal composition

Element	**Wt., %**
Fe	98.06
Mn	0.32
V	0.05
Ti	0.11
Si	0.62
Cr	0.38
S	0.33
P	0.12

Table (5) shown that, XRF analysis for slag composition. It appears that the produced slag can be considered as a primary material to produce titanium pigment. It can upgrade the titanium dioxide content by physical beneficiation to reduce the used chemicals in further processes.

Table 5: XRF analysis of slag composition

Oxide	**Wt., %**
TiO_2	77.59
FeO	9.86
SiO_2	2.73
Al_2O_3	3.47
MnO	1.09
CaO	1.89
MgO	1.14
Cr_2O_3	0.65
V_2O_5	0.53
P_2O_5	0.49
S	0.54

4. Conclusions

By increasing carbon content, the iron yield increased, but the rate of increasing decreased. Due to the increasing of titanium dioxide content in the slag. So, the efficiency of carbon almost does not change after a 20 % carbon assay. For that, increasing the carbon assay by more than 20 % isn't recommended.

Time has a remarkable effect on iron yield and carbon efficiency. Power consumption increases with increasing time, and so, the temperature. By increasing the temperature, the iron yield increases, and so, carbon efficiency.

The flux agent shows minor effect on iron yield. It has negative effect until assay around 2%, after that returns to values as without flux agent. It is due to the formation of calcium titanate. It increases the melting point of the slag and the viscosity.

The recommended optimum conditions level from the current study to smelting ilmenite by Maghara coal are 20% carbon assay at 30 minutes.

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دراسات على صهر المنيت الرمال السوداء المصرية باستخدام فحم المغارة

الملخص العربي:

الرمال السوداء هي رواسب شاطئية تأتي من منابع نهر النيل، وهي غنية بالمعادن الثقيلة. يعتبر الإلمنيت هو المعدن الاقتصادي الرئيسي ويمثل حوالي ٦٠ – ٧٠٪ من كمية المعادن الاقتصادية بها. ولزيادة القيمة المضافة للموارد الوطنية، تم إجراء سلسلة من التجارب لدراسة عملية الصهر لإنتاج خبث التيتانيا العالي والحديد الزهر. وقد تم خلال البحث دراسة تأثير العديد من العوامل مثل الزمن (٢٠، ٢٥، ٣٠ دقيقة)، محتوى الكربون (١٥٪، ٢٠٪، ٣٠٪) واستخدام محسنات الصهر (١٪، ٢٪، ٣٪) على الانتاجية. وقد أظهرت النتائج أن زمن التجربة له التأثير الأكبر على إنتاجية الحديد من بين العوامل الأخرى. وقد بينت الدراسة أن أقصى نسبة استعادة للحديد تم الوصول إليها كانت حوالي ٨٠,٥٪ مع تركيز لثاني أكسيد التيتانيوم في خبث التيتانيا حوالي ٧٧,٦٪ عند عوامل التجربة التالية: ٣٠٪ كربون لمدة ٣٠ دقيقة.