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Synthesis of Iron Oxide Pigments from Workshops Scrap Iron

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***Abstract*— Inorganic pigments are used in Sudan in many types of paints and they are imported. In the present study Scrap Iron (Industrial waste) was reacted with concentrated sulphuric acid to give ferrous sulphate compound. Ferrous sulphate was divided into two portions. The first portion was calcinated in oil fired oven at 750℃ for 3 hours and the yield was red iron oxide pigment. The second portion was treated with Sodium carbonate and the result is yellow iron oxide with air mixing and brown iron oxide without air mixing .Seven samples of yellow iron oxide were prepared. Temperature was adjusted to 200℃ in the same oven and the six samples were put in the oven with the first sample untreated. The second sample was heated for one hour, third sample two hours, till the sixth sample which was kept for five hours. Ranges of red colour iron oxide pigments were obtained.**

***Index Terms*— Ferrous sulphate, calcination.**

I. INTRODUCTION

Pigments are defined as colorants that are relatively insoluble in the medium in which they are applied. Pigments are used with binders (1).They differ from dyes that they are either transparent or opaque (Dyes are only transparent. (2)

Pigments can be classified as organic or inorganic, natural or synthetic. The most important pigments now are synthetic organic pigments and synthetic inorganic pigments and naturally occurring inorganic pigments (3).

Inorganic pigments can be grouped according to their chemical composition where organic pigments can be broken into two major categories azo and non-azo pigments. (4)

Inorganic pigments (Synthetic) are my field of research. In Sudan we import red pigments specially the iron red oxide pigments. Red iron oxide pigments are used in metallic door and windows in buildings to stop rusting then the final color is applied. Iron oxide red is available in many countries like India ,Iran,

Most of synthetic iron oxide is manufactured from iron and sulphuric acid (Bayer the German Company)(5).. This technology is used in this research but the only difference is the use of scrap iron waste collected from iron processing workshops in Khartoum North (Sudan).Success in producing iron oxide helps in improving the environment and saving hard currency.

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II. MATERIALS AND METH-ODS:

A. Material:

1-Iron scrap from workshops with iron contenet≈95%
2-Sulphuric acid (Industrial grade 98%)
3-Sodium carbonate
4-Tin (II) Chloride (100mg/l solution)
5-Mercuury (II) Chloride (100mg/l solution)
6-Phosphoric acid
7-Barium Diphenylamine Sulphonate
8-Potasium Dichromate (0.1N solution)
9-Ammoniumthiocynate (170ml/L solution)
10-Potasium permanganate (0.1N solution)

B. Methods:

1) Iron oxides

Preparation of the raw material for iron oxide pigment Iron (59m; 1.1mol) and sulphuric acid (98gram; 1mol).Scrap iron .after reaction completion ferrous sulphate is filtered from impurities (132gram).

This experiment is scaled to help in calculating manufacturing cost. In the scaling up 10Kg of iron and 17Kg of sulphuric acid were put in thick plastic barrel. This mixture is kept for four days with manual stirring. Filtration is carried after complete conversion to ferrous sulphate. The yield (22Kg) is kept for 26 days to evaporate water.

2) Precipitation method with stirring:

Alkali is added to ferrous sulphate Solution (2Kg of ferrous sulphate was dissolved in 10 liters of water and 3 Kg of Sodium carbonate dissolved in 15 liters of water)

3) Process:

The soda ash solution is slowly added to ferrous sulphate solution keeping it stirred by compressed air. The precipitate is filtered; washed and dried it gave the yellow synthetic iron oxide (sample 7).

4) Precipitation without stirring method:

This is similar to the previous method in alkali preparation and ferrous sulphate but without stirring .2 Kg of ferrous sulphate is dissolved in 10 liters of water and 3 Kg of Sodium carbonate dissolved in 10 liters of water were mixed without stirring for 2 days .Supernatant liquid was pumped out till a viscous paste of ferrous hydroxide is formed. It is left for air drying so that the atmospheric oxygen will oxidize ferrous hydroxide to ferric oxide where the brown pigment is formed and the yield is 1Kg of ferric oxide.

5) *Calcination of Ferrous sulphate:*

Calcination was carried out in oil fired oven at a temperature 750 °C for 10Kg of ferrous sulphate for 36 hours and the yield after pulverizing and drying was 2.5 kg

Determination of total Iron expressed as Iron (III) oxide

1-Hydrochloric acid conc.
2- Tin(II) chloride 100g/1 solution
3- Dissolve 50g of $SnCI_2.2H_2O$ in 300ml of hydrochloric acid and then dilute with water to 500ml
4- Mercury (II) chloride solution (60 to 100g/I)
5- Mixture of sulphuric acid and phosphoric (150mI from each each acid are diluted with water
6- Diphenylamine mixed with sulphuric acid (1g of barium diphenylaminesulphonate in 100mI of sulphuric acid
7- Potassium dichromate 0. 1N solution
8- Ammonium thiocynate 170g/I solution
9- Potassium permanganate 0.1N solution

C. *Procedure:*

One gram of the sample was weighed the sample is placed in 400ml beaker with watch glass and heated 90C till a clear solution was formed Tin (II) chloride was added potassium permanganate should be added till a yellow color is seen then Tin (II) chloride is added till color disappears .

The complete reduction of iron is confirmed by a drop of ammonium thiocynate consequently no red color is seen.

The solution is diluted with 200mI of water with 15mI of mercury (II) chloride (4) all at once with vigorous stirring White precipitate appeared 50mI of sulphuric/phosphoric mixture (5) and 3 drops of diphenylamine solution (6) are added Titration with potassium dichromate solution (7) and the end point is when the dark green color is changed to violet.

The formula with which the iron oxide percentage is calculated is percentage of iron (III) oxide =0.7984V/m where V is the volume of potassium permanganate solution in milliliters & m is the sample mass.

Determination of Fe (III) percentage in the calcined mass (Red) Titration results are 115, 116, 118, 118, mls with average 116.75mI percentage of Fe (III)=0.798x116.75=93.1165%

Calcination of ferric oxide (Red)

Calcination of yellow ferric oxide gave light red for first stage and calcination continued and after every one hour. A sample was taken and cooled.

D. *Process:*

Seven samples of yellow ferric oxide are calcinated as follows (temperature is kept at 200^0C throughout the six experiments) . The first [sample is untreated while the other are treated as follows.

The second sample kept in 200^0C for one hour ,the third two hours at the same temperature till the sixth one is kept at 200^0C for five hours these calcination were done on a laboratory electrical oven (see appendix)

Air mixing (Yellow)

End points in Titration were 100mI , 102mI, 109mI, 101mI excluding 109mI the average relation to calculate percentage iron as Fe (III) 0.798x101mI= 80.598%

(2) – Brown (without air mixing)

End points in titration were 94, 95, 95, 94.5 mI the average is 94.6 there using the previous relation for the determination of Fe (III) percentage the following result was obtained 0.798+94.6=75.49%

Determination of water soluble matter in pigments

Tow gram of the pigment was taken and weighed accurately then washed with distilled water and dried in an oven with temperature 105C and this was repeated three times The percentage was calculated as follows .

Weight of original sample-Weight of washed and dried Sample100%
Weight of original

1-Yellow :

Weight of sample=2gram

Weight after three successive washing (1.98 1.98, 1.97) and the average is=1.976

% of Weight loss=type=2-1.976 100/2=1.1% ie type 2

Brown

Weight of sample=2gram

Weight after three successive washing (1.99, 1.98, 1.98) and the average -is 1.98

% of Weight loss (water soluble matter)=type=2-1. 98 100/2=1%

Red

Weight of sample=2gram

Weight after three successive washing (1.99, 1.99, 1,98)g and the average is=1.986g

% of Weight loss (water soluble matter)=type=2-1 . 986 100/2=0.7%

III. RESULTS:

Table for percentage ferric (III)oxide content and water soluble mater content

Table No (1)

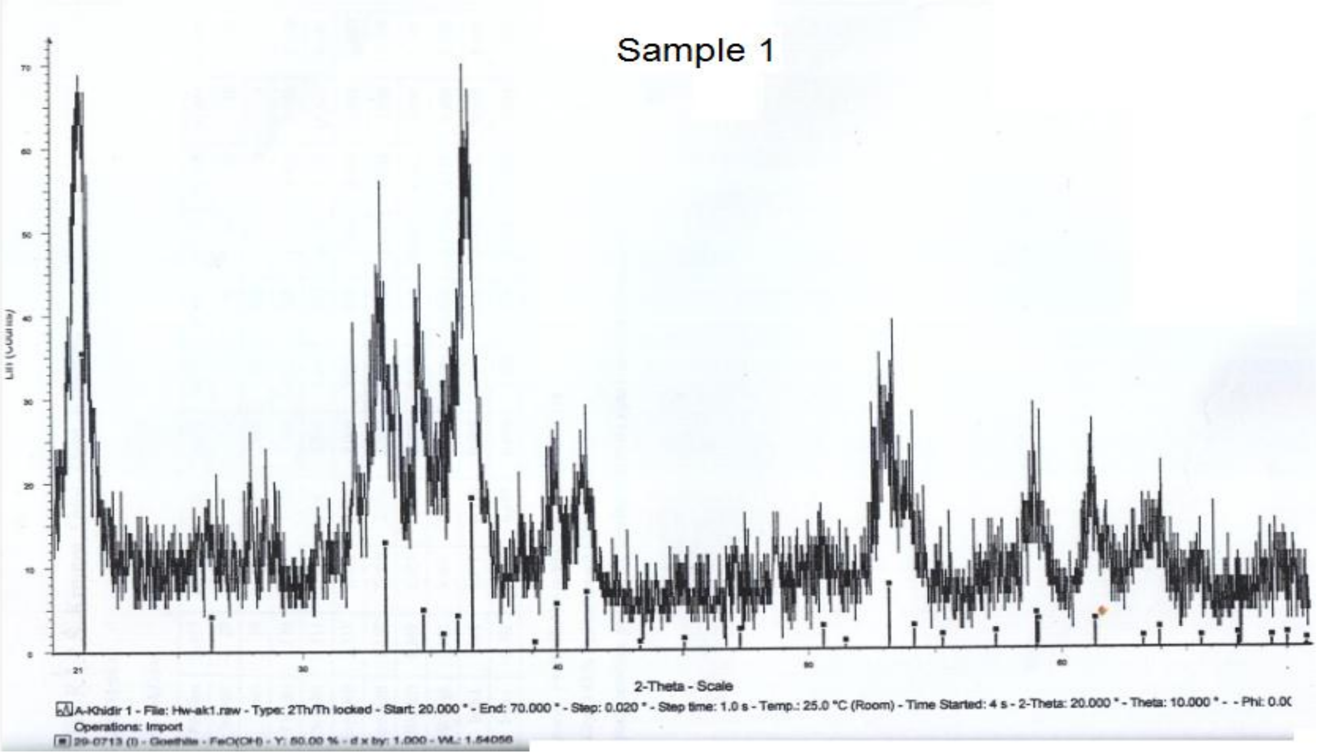
Material	%Fe(III) content	%soluble mater content
Red sample	93.1165	0.7
Yellow sample	80.59	1.1
Brown sample	75.49	1

Results of X-Ray powder diffraction(X-RD)

WinFit! R.1.2S. Krumm, Geol.Dept.Erlangen
File: c:\hw-ak1 raw

Position	33.087	27.241	39.931	34.621	34.552	39.931	53.101	58.949	61.034	63.448
Int.max	29	201	98	111	111	98	10	12	10	10
Area	39	251	122	139	139	122	2	20	1	1
FWHM	1.120	1.020	1.020	1.020	1.020	1.020	0.172	1.436	0.120	0.120
Int.breadth	1.351	1.245	1.245	1.245	1.245	1.245	0.210	1.618	0.146	0.146
Expo.left	2.135	2.000	2.000	2.000	2.000	2.000	2.000	3.969	2.000	2.000
Expo.right	2.165	2.000	2.000	2.000	2.000	2.000	2.000	5.165	2.000	2.000
WHM.left	0.869	0.551	0.456	0. 490	0.456	0.4560	0.092	0207	0.040	0.040
WHM.right	0.251	0469	0.564	0.530	0.564	0.564	0.080	1.229	0.080	0.080
beta 1	1.049	0.672	0.556	0.598	0.556	0.556	0.112	0.231	0.049	0.049
Beta. r.	0.302	0.573	0.689	0.646	0.688	0.689	0.098	1.388	0.098	0.098

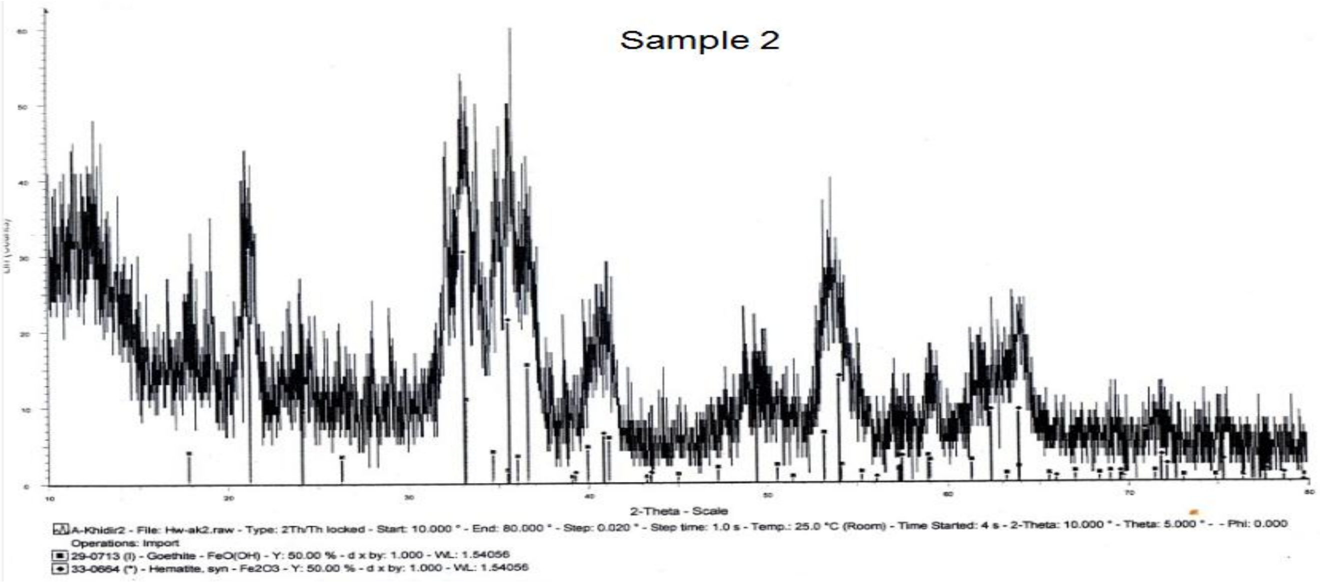
Background: $y = 0.000x^3 + 0.000x^2 + -11.695x + 695.118$
Reliability 73.47% Residual error 0.67829347 %
No Alpha**2**- correction; positions and breadths refer to the alpha2-components



WinFit! R.1.2S. Krumm, Geol.Dept.Erlangen
File: c:\hw-ak2 raw

Position	33.087	27.241	39.931	34.621	34.552	39.931	53.101	58.949	61.034	63.448
Int.max	29	201	98	111	111	98	10	12	10	10
Area	39	251	122	139	139	122	2	20	1	1
FWHM	1.120	1.020	1.020	1.020	1.020	1.020	0.172	1.436	0.120	0.120
Int.breadth	1.351	1.245	1.245	1.245	1.245	1.245	0.210	1.618	0.146	0.146
Expo.left	2.135	2.000	2.000	2.000	2.000	2.000	2.000	3.969	2.000	2.000
Expo.right	2.165	2.000	2.000	2.000	2.000	2.000	2.000	5.165	2.000	2.000
WHM.left	0.869	0.551	0.456	0. 490	0.456	0.4560	0.092	0207	0.040	0.040
WHM.right	0.251	0469	0.564	0.530	0.564	0.564	0.080	1.229	0.080	0.080
beta 1	1.049	0.672	0.556	0.598	0.556	0.556	0.112	0.231	0.049	0.049
Beta. r.	0.302	0.573	0.689	0.646	0.688	0.689	0.098	1.388	0.098	0.098

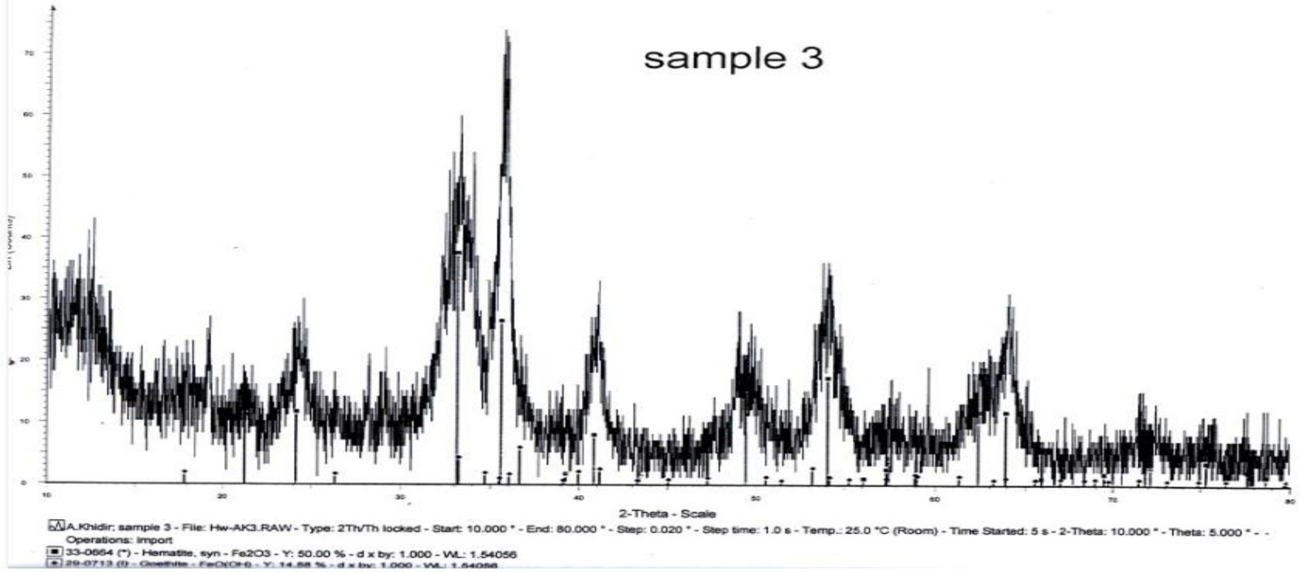
Background: y=0.000x^3 + 0. 000x^2 + -11.695x + 695.118
Reliability 73.47% Residual error 0.67829347 %
No Alpha**2**- correction; positions and breadths refer to the alpha1-and alpha2-components



WinFit! R.1.2S. Krumm, Geol.Dept.Erlangen
File: c:\hw-ak3 raw

Position	19.076	24.193	41.283	40.800	49.393	54.414	63.683
Int.max	10	13	34	39	10	10	10
Area	39	251	122	139	139	122	2
FWHM	1.120	1.020	1.020	1.020	1.020	1.020	0.172
Int.breadth	1.351	1.245	1.245	1.245	1.245	1.245	0.210
Expo.left	2.000	2.000	2.000	2.000	2.000	2.000	2.000
Expo.right	2.000	2.000	2.000	2.000	2.000	2.000	2.000
WHM.left	0.040	0.040	0.541	0.230	0.040	0.097	0.040
WHM.right	0.080	0.080	0.299	0.340	0.080	0.080	0.109
beta 1	1.049	0.672	0.556	0.598	0.556	0.556	0.112
Beta. r.	0.302	0.573	0.689	0.646	0.688	0.689	0.098

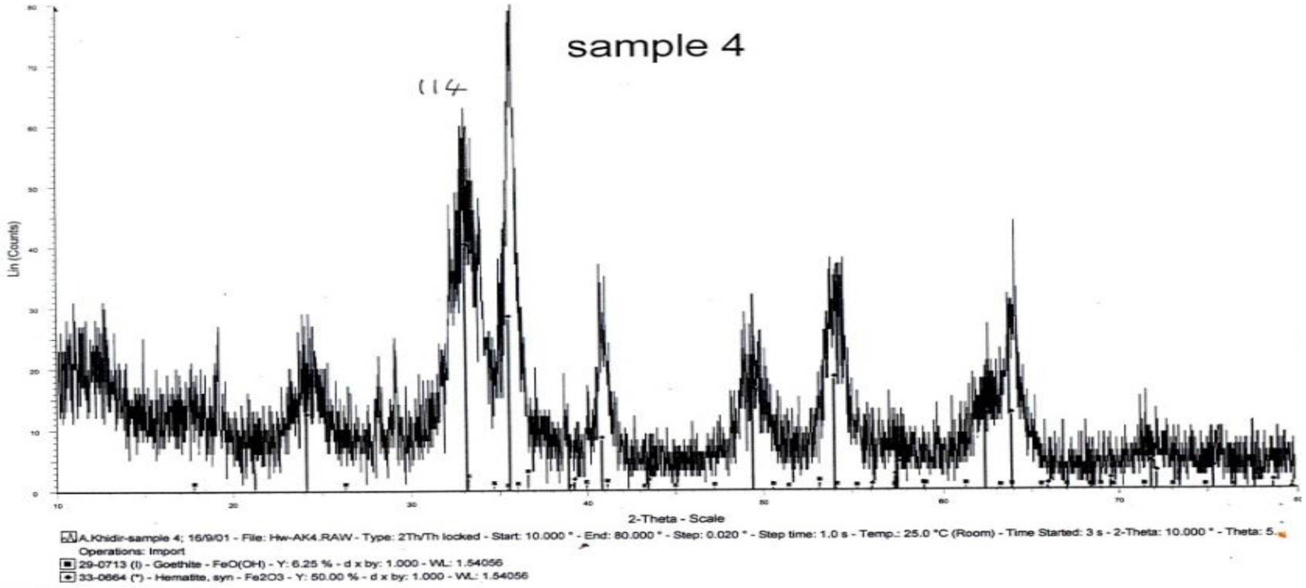
Background: y=0.000x^3 + 0. 000x^2 + -0.050x + 12.100
Reliability 100% Residual error 0.0000000 %
No Alpha**2**- correction; positions and breadths refer to the alpha1-and alpha2-components



WinFit! R.1.2S. Krumm, Geol.Dept.Erlangen
File: c:\hw-ak4 raw

Position	24.579	33.366	40.607	49.490	53.834	63.490
Int.max	150	60	391	427	453	482
Area	4	1	58	1	3	122
FWHM	0.153	0.120	0.760	0.120	0.134	1.020
Int.breadth	0.187	0.146	0.927	0.146	0.163	1.245
Expo.left	2.000	2.000	2.000	2.000	2.000	2.000
Expo.right	2.000	2.000	2.000	2.000	2.000	2.000
WHM.left	0.530	0.283	0.443	0.495	0.467	0.415
WHM.right	0.490	0.137	0.577	0.525	0.553	0.605
beta 1	0.089	0.049	0.437	0.049	0.049	0.556
Beta. r.	0.089	0.098	0.490	0.098	0.114	0.689

Background: y=0.000x^3 + 0. 000x^2 + -0.050x + 12.100
Reliability 100% Residual error 0.0000000 %
No Alpha**2**- correction; positions and breadths refer to the alpha1-and alpha2-components

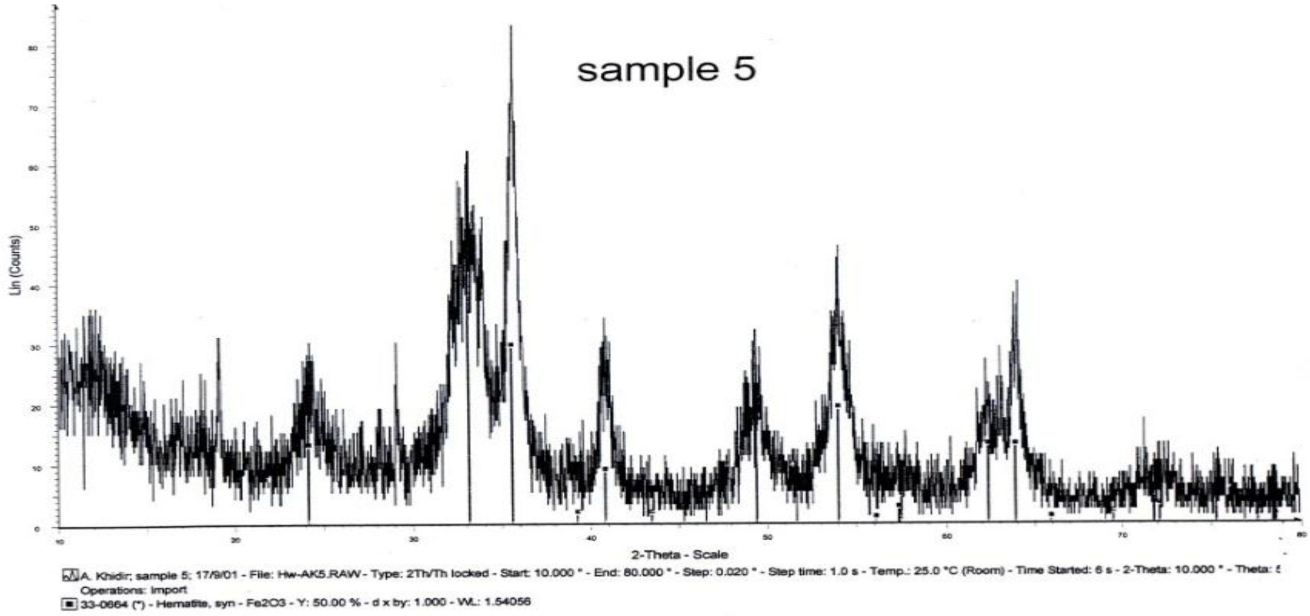


A.Khidir-sample 4; 16/9/01 - File: Hw-AK4.RAW - Type: 2Th/Th locked - Start: 10.000 ° - End: 80.000 ° - Step: 0.020 ° - Step time: 1.0 s - Temp.: 25.0 °C (Room) - Time Started: 3 s - 2-Theta: 10.000 ° - Theta: 5.
Operations: Import
29-0713 (I) - Goethite - FeO(OH) - Y: 6.25 % - d x by: 1.000 - WL: 1.54056
33-0664 (*) - Hematite, syn - Fe2O3 - Y: 50.00 % - d x by: 1.000 - WL: 1.54056

WinFit! R.1.2S. Krumm, Geol.Dept.Erlangen
File: c:\hw-ak5 raw

Position	24.455	40.607	49.779	62.331	64.166
Int.max	9	10	10	10	10
Area	4	1	2	1	1
FWHM	0.421	0.120	0.140	0.120	0.120
Int.breadth	0.501	0.146	0.170	0.146	0.146
Expo.left	2.466	2.000	2.000	2.000	2.000
Expo.right	1.099	2.000	2.000	2.000	2.000
WHM.left	0.406	0.040	0.060	0.040	0.040
WHM.right	0.014	0.080	0.080	0.080	0.080
beta 1	0.480	0.049	0.073	0.049	0.049
Beta. r.	0.021	0.098	0.098	0.098	0.098

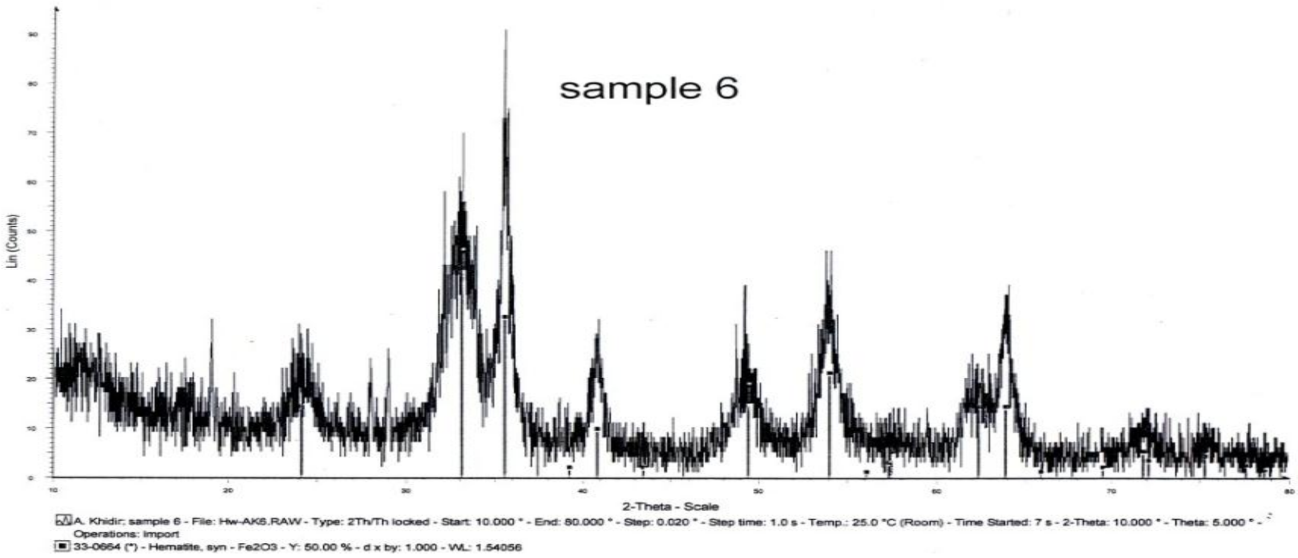
Background: y=0.000x^3 + 0. 000x^2 + -0.050x + 12.100
Reliability 100% Residual error 0.0000000 %
No Alpha**2**- correction; positions and breadths refer to the alpha1-and alpha2-components



WinFit! R.1.2S. Krumm, Geol.Dept.Erlangen
File: c:\hw-ak6 raw

Position	24.178	40.703	49.200	53.834	63.779
Int.max	11	10	10	10	10
Area	8	2	1	1	1
FWHM	0.496	0.138	0.120	0.120	0.120
Int.breadth	0.774	0.169	0.146	0.146	0.147
Expo.left	1.002	2.000	2.000	2.000	2.000
Expo.right	1.018	2.000	2.000	2.000	2.000
WHM.left	0.241	0.040	0.040	0.040	0.040
WHM.right	0.255	0.098	0.080	0.080	0.080
beta 1	0.378	0.049	0.049	0.049	0.049
Beta. r.	0.396	0.120	0.098	0.098	0.098

Background: y=0.000x^3 + 0. 000x^2 + -0.050x + 12.100
Reliability 100% Residual error 0.0000000 %
No Alpha**2**- correction; positions and breadths refer to the alpha1-and alpha2-components



Analysis of calcinated samples is done by X-Ray powder Diffraction (X-RD) data was recorded with a Siemens D500 Diffractometer using Cu-Kα radiation (λ=1.5406) The crystallite (particle) size of α-Fe_2O_3 ions determined from X-Ray diffraction data using the Scherrer equation (using X-RD graphs at the appendix) .

T= Cλ/Bcosθ

T=crystallite size

C=Factor (0.9-1) taken as 0.9 in this case.

λ =Wavelength in A^0

B=Full width at half maximum (FWHM) =U-S where S=0.1360(Instrumental correction) should be corrected to radians as well as U

Θ=Angle (2θ is taken from the results)

Effect of heat on chemical structure and color on iron oxide

Table (2)

Sample number	Sample name	Chemical structure
0	Goethite	Fe O(OH)
1-hr at 200^0C	Goethite	Fe O(OH)
2-hr at 200^0C	Goethite Hematite	Fe O(OH)Fe_2O_3
3-hr at 200^0C	Goethite Hematite	Fe O(OH){14.58%}sFe_2O_3
4-hr at 200^0C	Goethite Hematite	Fe O(OH){6.25%}Fe_2O_3
5-hr at 200^0C	Hematite	Fe_2O_3
6-hr at 200^0C	Hematite	Fe_2O_3

Calculation of Crystallite Size Using Sherrer Equation (T= Cλ/Bcosθ)

Table No (3)

Sample-0	U	$B(U-S)^0$ S=0.136	B in Radians	θ	Cos θ	**Crystallite Size (μ) Cλ/Bcosθ**
0	0.17	0.034	$1.18x10^{-3}$	6.1	0.998	119
1	1.020	0.894	$3.12x10^{-2}$	13.62	0.971	4.6
2	1.020	0.894	$3.12x10^{-2}$	13.62	0.971	4.6
3	1.120	0.994	$3.42x10^{-2}$	9.5	0.986	4.6
4	0.153	0.027	$9.42x10^{-4}$	12.25	0.977	150
5	0.421	0.285	$9.9x10^{-3}$	12.22	0.977	1.6
6	0.496	0.36	$1.2x10^{-2}$	12.08	0.978	1.06

The identification were only for the 110 peak in all samples

IV. DISCUSSION:

From result analysis it is clear that prolonged heating except sample (4) the only deviation from the rule reduces particle size. In pigment manufacture the particle size is one of the most important properties in which the luster and depth of hue is attributed to. Cyclones are used in particle size reduction and they consume energy in doing that, so by calcination one can reduce energy consumption and then complete size reduction in cyclone. Secondly five pigment colors were obtained from scrap iron

The use of X-RD helped in getting reliable results

V. CONCLUSION:

We are all continually faced with a series of great opportunities brilliantly disguised as insoluble problems. Accumulation of scrap iron was environmental hazards which changed to useful goods in this research.

Results obtained showed clearly the possibility of producing pigments (Red, Yellow, Brown) using scrap iron and sulphuric acid and sodium carbonate. Consequently hard currency saving and environmental cleaning from iron scrap.

ACKNOWLEDGMENTS:

In this research particle size and chemical structure (X-RD) were done in UK with the help of Dr. Husham Wadat Allah (University of Khartoum Physics Department) so I thank him for the help.

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