Change in Chloride Content of Regenerated Red Iron Oxide Particles in Accordance with Particle Sizes

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***Abstract* — Red iron oxide which is produced by regeneration of waste hydrochloric acid from steel pickling line contains chloride. Chloride has negative effects on industrial productions which use red iron oxide as a raw material.**

This paper asserts red iron oxide particles have different chloride content according to their particle size. Regenerated red iron oxide was sampled from different production batches and these samples were grouped according to their particle size with sieving them from 1 mm to 75 µm. Sieved red iron oxide samples were analysed with spectrophotometer to determine chloride content.

The study found out that chloride content slightly increased by increasing particle size up to 710 µm, after that size chloride content was drastically increased, such that, removing particles bigger than 1 mm from the iron oxide provides a 11,97 % reduction of the total chloride content and causes only 0,27 % loss from the total material.

***Keywords:* Regeneration Red Iron Oxide; Chloride; Particle Size, Steel Pickling, Hematite.**

I. Introduction

Pickling plants are production lines where the oxide layer on hot rolled coils is cleaned in acid baths. In this line, the oxidized surfaces of the coils are cleaned and prepared for further processes. During pickling process, used acid is contaminated with iron chloride. This waste acid is regenerated in acid regeneration plant (ARP) in order to re-use.

In ARP, waste acid is regenerated to remove iron and this reaction is given in formula (1) and (2) [1]

$$4FeCl_2 + 4H_2O + O_2 \rightarrow 2Fe_2O_3 + 8HCl \quad (1)$$

$$2FeCl_3 + 3H_2O \rightarrow Fe_2O_3 + 6HCl \quad (2)$$

Oxygen and evaporated water convert metal chlorides into oxides and HCl. The solid particles (Fe_2O_3) will fall down to the lower cone of the reactor in the form of powder and are discharged through a rotary valve which keeps gases inside of the reactor separated from the outside atmosphere [2, 3].

As explained above; metal oxide product decomposes completely into red α-Fe_2O_3 powders. The recovery of α-Fe_2O_3 is not only economic demand, but also an environmental necessity [4]. Although this metal oxide is defined as waste, it is semi-finished or by-product for some sectors directly or indirectly. Over the years, intensive R&D activities have led to enhancements in physical and chemical properties of iron oxides. These products are increasingly finding wide applications across various industries such as use of iron oxide in water treatment & purification and in chemical processing as catalyst are anticipated to offer new opportunities of growth of value-added iron oxide products [5]. In additionally, spray roasted iron oxides have been used on an industrial scale for the production of soft and hard ferrites on an industrial scale at steel mills in Japan, USA and Europe since the year 1964 [6].

One of the negative characteristic of red iron oxide powder is its chloride content for the mentioned industrial usage. Reducing the chloride content in regenerated iron oxides by an economical procedure, without significantly changing the ferric oxide quality is believed to be one of the most critical issues for the development of regenerated iron oxides as commercially useful raw materials [7].

Kohno (1992) reported how some of characteristic of spray roasted iron oxide can be controlled by the operation of the HCl regeneration roaster. Such properties as particle size, oxide diameter, pressed compact density and chloride content can be improved by selection of conditions in the ARP [8].

Ruthner M. J. (2014), explained washed iron oxides exhibiting total chloride levels in the order of 600 ppm Cl^- are available. Further washing results in Cl^- levels of 300 ppm and an additional thermal treatment, by means of a short treatment within a vertical un-obstructed furnace, yields iron oxides with < 20 ppm Cl^- [9].

Itoh S. (1976) explained that red iron oxide particles are formed around droplets of acid as spherical shell during the regeneration of waste acid [10] (Fig. 1).

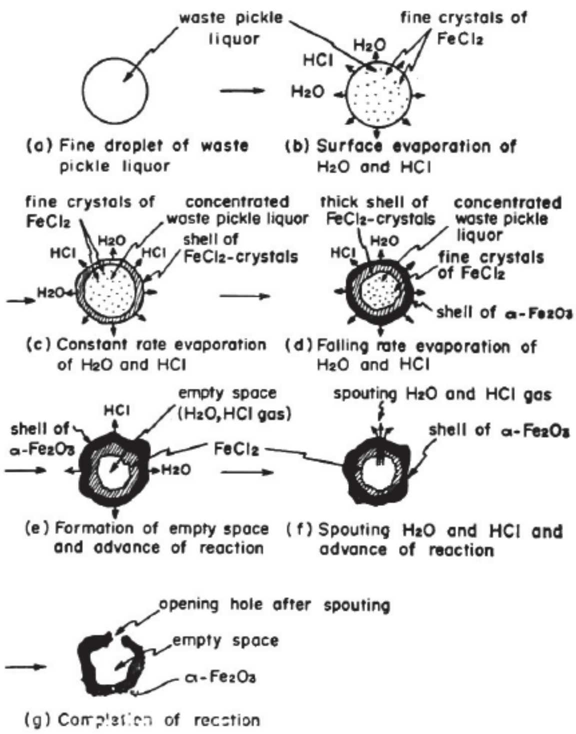

Fig. 1 Formation scheme of granulated roaster hematite from droplet of waste acid

Red iron oxide analysed under SEM and their images had been taken (Fig. 2). According to images, particle structure of iron oxides is a mixture of cracked and uncracked spheres where uncracked particles are bigger and may keep more chloride than the cracked ones. This study is based on mentioned theory and aims to prove it.

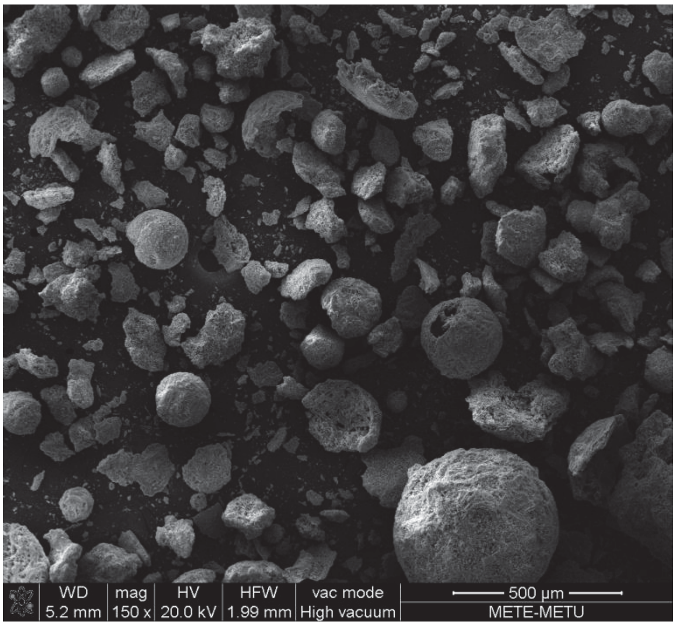

Fig. 2 SEM Image of Red Iron Oxide

II. EXPERIMENTAL STUDIES

G. *Materials*

Iron oxides, used in this study are produced by pickling line of MMK Metalurji & Liman İşletmeciliği A.Ş. Technical data sheet of Iron oxides is given in Table-1.

TABLE-1

RED IRON OXIDE TECHNICAL DATA SHEET

	No	Property	Value
Iron Oxide is the product of Acid Regeneration Plant	1	Fe_2O_3	Min 98,5
	2	MnO	0,2 (± 0,10)
	3	SiO_2	Max 0,15
	4	Al_2O_3	Max 0,08
	5	TiO_2	< 0,03
	6	Cr_2O_3	< 0,05
	7	Na_2O	< 0,04
	8	K_2O	< 0,01
	9	CaO	< 0,01
	10	MgO	< 0,01
	11	P_2O_5	< 0,02
	12	SO_3	< 0,01
	13	LOI	0.95
	14	Chloride %	< 0,5
	15	Bulk Density, g/cm^3	< 0,5
	16	Moisture @ 105ºC , %	< 1
	17	pH @ 10% Suspension	3 (± 0,5)

H. *Devices and equipment*

Iron oxide was sieved with Fritsch brand sieves + 1 mm, + 710 µm, + 500 µm, + 250 µm, + 150 µm, + 100 µm, + 75 µm.[13] AND brand GR200 model precision scales (0,0001g precision) were used for weighing samples. Iso lob brand filters and DR 5000 Brand spectrophotometer were used for chloride analyses. Elektro-Mag 30x45 Brand heating plate was used to heat.

İ. *Chemicals*

Merck Brand Analytical grade 99,5% NaCl, 99% Ammonium iron (III) sulphate dodecahydrate ($(NH_3)Fe(SO_4)_3.12H_2O$, 99% Mercury (II) c ($Hg(SCN)_2$), 65% Nitric Acid (HNO_3) and SIGMA- ALDIRICH brand 99,8% Ethanol (C_2H_5OH) was used to prepare solutions. Ultra high pure water, which was produced with MES 08 brand device was used.

J. *Test and Assessment Method*

Samples were prepared according to TS ISO 11648-2 [11]. Iron oxide samples, taken from different production batches, were sieved with +1mm / +710 µm / +500 µm / +250 µm / 150 µm / +100 µm and +75 µm sieves and each amount of iron oxide, refuse of sieve, were weighed. The sieving process was carried out using the FRITSCH brand screens in FRITSCH sieving machine which conformed with TS ISO 3310-1 [12] that's shown in Fig. 3.

Fig. 3 Fritsch Sieves

According to sieve size, chloride content of each batch was analysed. To analyse chloride content, 1,000 g iron oxide was heated in 100 ml water, after boiling point, mixture is cooled down and filtered with membrane filter. Chloride content of iron oxide was analysed with spectrophotometer under method of 0-1-2-5-10-15-20-30 mg/L calibration graph and 455 nm wave length. Chloride content measured in Hach DR 5000 Spectrophotometer which shown in Fig. 4.

Fig. 4 Hatch DR 5000 Spectrophotometer

III. RESULTS

Percentage of sieve fraction and chloride content are given in Table-2 for the iron oxides from 12 different batches and sieved between +1mm, -75 µm.

TABLE -2

PARTICLE SIZE DISTRIBUTION AND CHLORIDE CONTENT

No	Sample Date	Batch No	Sieve Size	Quantity %	Cl^- % Content
1	22.07.2016	16RIO2107B003	+ 1 mm	0.17	20.37
			+710 µm	2.20	0.99
			+500 µm	10.80	0.45
			+250 µm	15.00	0.33
			+150 µm	27.33	0.32
			+100 µm	20.67	0.27
			+75 µm	19.66	0.30
			-75 µm	4.17	0.25
2	02/08/2016	16RIO0208B001	+ 1 mm	0.17	14.90
			+710 µm	2.40	0.46
			+500 µm	11.60	0.31
			+250 µm	23.00	0.27
			+150 µm	27.50	0.28
			+100 µm	16.17	0.24
			+75 µm	14.00	0.33
			-75 µm	5.16	0.30
3	05/08/2016	16RIO0508B002	+ 1 mm	0.50	17.80
			+710 µm	7.00	0.81
			+500 µm	14.00	0.38
			+250 µm	36.50	0.24
			+150 µm	20.50	0.20
			+100 µm	9.83	0.18
			+75 µm	7.17	0.22
			-75 µm	4.50	0.25
4	10/08/2016	16RIO1008B008	+ 1 mm	1.00	18.93
			+710 µm	7.90	1.02
			+500 µm	24.10	0.30
			+250 µm	51.83	0.23
			+150 µm	7.33	0.22
			+100 µm	3.17	0.21
			+75 µm	2.00	0.24
			-75 µm	2.67	0.35
5	02/09/2016	16RIO0209B005	+ 1 mm	0.17	15.48
			+710 µm	4.70	0.43
			+500 µm	15.30	0.21
			+250 µm	36.83	0.19
			+150 µm	19.00	0.19
			+100 µm	11.33	0.18
			+75 µm	6.84	0.19
			-75 µm	5.83	0.20
6	05/09/2016	16RIO0509B005	+ 1 mm	0.17	12.93
			+710 µm	5.80	0.49
			+500 µm	13.20	0.18
			+250 µm	38.33	0.10
			+150 µm	20.00	0.11
			+100 µm	10.67	0.10
			+75 µm	6.67	0.08
			-75 µm	5.16	0.08

No	Sample Date	Batch No	Sieve Size	Quantity %	Cl^- % Content
7	06/10/2016	16RIO0610B006	+ 1 mm	0.16	14.86
			+710 µm	1.80	0.87
			+500 µm	13.00	0.22
			+250 µm	47.30	0.13
			+150 µm	23.64	0.15
			+100 µm	6.50	0.14
			+75 µm	4.30	0.19
			-75 µm	3.30	0.23
8	07/10/2016	16RIO0710B005	+ 1 mm	0.05	18.92
			+710 µm	3.95	1.43
			+500 µm	19.17	0.31
			+250 µm	47.33	0.25
			+150 µm	19.00	0.27
			+100 µm	5.00	0.33
			+75 µm	3.33	0.44
			-75 µm	2.17	0.49
9	11/10/2016	16RIO1110B006	+ 1 mm	0.17	25.63
			+710 µm	9.16	2.93
			+500 µm	15.17	0.45
			+250 µm	34.50	0.24
			+150 µm	21.50	0.29
			+100 µm	10.00	0.31
			+75 µm	3.83	0.40
			-75 µm	5.67	0.52
10	26/10/2016	16RIO2610B008	+ 1 mm	0.35	16.80
			+710 µm	8.50	1.33
			+500 µm	15.67	0.49
			+250 µm	48.15	0.24
			+150 µm	16.83	0.28
			+100 µm	5.17	0.30
			+75 µm	2.50	0.35
			-75 µm	2.83	0.43
11	09/11/2016	16RIO0811B008	+ 1 mm	0.01	17.18
			+710 µm	3.63	0.70
			+500 µm	10.03	0.40
			+250 µm	40.00	0.20
			+150 µm	26.67	0.21
			+100 µm	8.50	0.27
			+75 µm	5.50	0.37
			-75 µm	5.66	0.56
12	10/02/2017	17RIO1002B007	+ 1 mm	0.33	31.02
			+710 µm	10.00	9.75
			+500 µm	4.83	1.52
			+250 µm	20.83	0.61
			+150 µm	24.50	0.56
			+100 µm	12.50	0.52
			+75 µm	10.84	0.57
			-75 µm	16.17	0.83

For 12 batches, average percentage of sieve fraction and chloride content is given in Table-3.

TABLE 3

AVERAGE PARTICLE SIZE DISTRIBUTION AND CHLORIDE CONTENT

Sieve Size	% Quantity	% Cl^-
+ 1 mm	0,27	18,74
+710 µm	5,59	1,77
+500 µm	13,91	0,44
+250 µm	36,63	0,25
+150 µm	21,15	0,26
+100 µm	9,96	0,25
+75 µm	7,22	0,31
-75 µm	5,27	0,37

According to the data given in Table-3, red iron oxide particles' sizes give a Gaussian distribution graphic, Fig. 5.

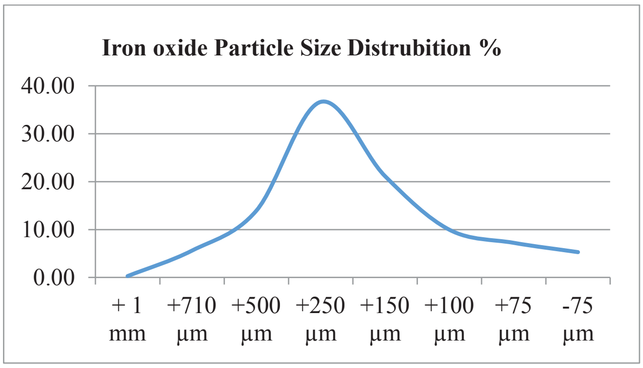

Fig. 5 Iron Oxide Particle Size Distribution %

Also particles bigger than 1 mm have highest chloride content. Chloride content decrease with the decreasing particle size, but gains a tendency to increase for the particles with a size smaller than 100 µm, Fig. 6.

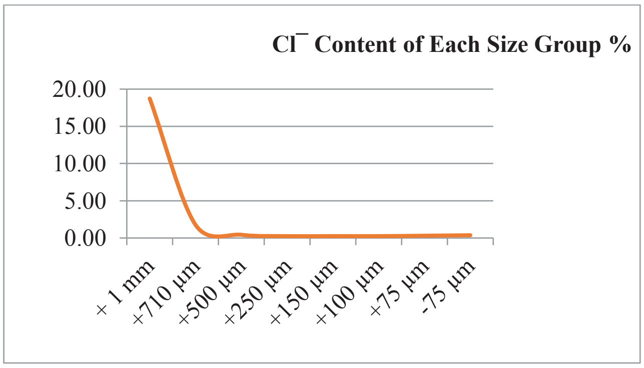

Fig. 6 Chloride Content of Each Size Group

Cl^- quantity for each size is given at Table 4. Total Cl^- in the sieved red iron oxide is 0,424 and it is the sum of the Cl^- quantity coming from each size. Cl^- % quantity for each size is calculated. For example for +1 mm size, Cl^- % Quantity = 0,51/0,424x100 = 11,97. Means, 0,27% of total red iron oxide particle size is bigger than 1 mm and the Cl^- in this size group is 11,97% of the total Cl^-.

TABLE 4

CHLORIDE QUANTITY FOR EACH SIZE

Sieve Size	Quantity %	Cl^- % Content	Cl^- Quantity for Each Size	Cl^- % Quantity for Each Size
+ 1 mm	0,27	18,74	0,051	11,97
+710 µm	5,59	1,77	0,099	23,29
+500 µm	13,91	0,44	0,060	14,27
+250 µm	36,63	0,25	0,092	21,82
+150 µm	21,15	0,26	0,054	12,80
+100 µm	9,96	0,25	0,025	5,97
+75 µm	7,22	0,31	0,022	5,22
-75 µm	5,27	0,37	0,020	4,655
		Total:	0,424	100,000

IV. CONCLUSIONS

The chloride contamination in the red iron oxide produced by pickling process waste hydrochloric acid regeneration is one of the most refusing factors for the further sectors which use it as a raw material. This study finds out that the bigger particles contain the higher chloride.

By removing particles bigger than 1 mm from the iron oxide provides a 11,97 % reduction on the total chloride content and causes only 0,27 % loss from the total material.

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REFERENCES

[1] Mmk Turkey Acid Regeneration Plant Main Data, DANIELI TRAINING CENTER, DANIELI & C SPA.
[2] Fouad N. E., Ismail H. M., Recovery of red iron oxide pigmentry powders from chemically modified steel pickling chemical waste, Journal Of Materials Science Letters 17 (1998)
[3] Ismail H. M., Zaki M. I., Hussein G. A. M. and Magar M. N., Powder Technology. 63 (1990) 87
[4] Devi A., Singhal A. and Gupta R., A Review on spent pickling liquor, Civil Engineering Department, Birla Institute of Technology & Science, International Journal Of Environmental Sciences Volume 4, No 3, 2013
[5] Iron Oxide Market; Paints and Coating to Surface as New Avenue for Iron Oxide Producer and Support Demand for the same over the Forecast Period: Global Industry Analysis and Opportunity Assessment, 2015 – 2025
[6] Goldman A, Modern Ferrite Technology 2nd Edition, 2005
[7] US005597547A, 1997, Reduction Of Residual Chloride In Iron Oxides, Inventor: Hamilton, Jr. David M., Assignee: Shell Oil Company

[8] Goldman A., Handbook of Modern Ferromagnetic Materials, Springer Science+Business Media, LLC, 1st Edition, 1999

[9] Ruthner M. J., 2014, Desired Development Aspects for Spray Roasted Iron Oxides Predominantly for the Production of Ferrites, J. Jpn. Soc. Powder Powder Metallurgy Vol. 61 Supplement, No. S1

[10] Itoh S., Endo I., Maki K., Kosaka A., 1976. "Ferric oxide produced by spray roasting of HCl pickling liquor", Tetsu-to-Hagane, 62(8), 1035-1044

[11] TS ISO 11648-2, Statistical aspects of sampling from bulk materials - Part 2: Sampling of particulate materials

[12] TS ISO 3310-1 Test sieves - Technical requirements and testing - Part 1: Test sieves of metal wire cloth