

## High Purity Ferric Oxide : Origin of Impurities and IROX-NKK Purification Process

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### ABSTRACT

A new process based on the co-precipitation method was developed for removing harmful impurities during Mn-Zn ferrite production such as SiO<sub>2</sub> and P from waste pickle liquor. By this process a final result of less than 100 ppm of SiO<sub>2</sub> and less than 10 ppm of P content in the ferric oxide is easily attained. Though Ca cannot be removed by this process, water rinsing of the ferric oxide is effective for reducing Ca content to less than 100 pm. For further purification, the origins of each impurity must be investigated and then taken away.

Key words :

### 1. Introduction

Ferric oxide is one of the major constituent materials of ferrites. In particular, high purity ferric oxide is indispensable for the production of high performance Mn-Zn ferrite cores.

This paper reports the results of our investigation into the origins of several impurities in ferric oxide and introduces our novel process for removing them.

### 2. Origin of Impurities in Ferric Oxide

As most ferric oxide for ferrites is a by-product of the hydrochloric acid regeneration process in a steel sheet pickling line, there are a lot of opportunities for it to be contaminated. Fig. 1 shows the outline of this process and the major sources of impurities. As shown in Fig. 1, alkali metal and alkaline earth metal come from industrial water, heavy metal comes from dissolved scale compositions of the pickled steel sheet and silicon comes from both.

Table 1. shows an example of our investigation into the origins of Si and Ca in the waste pickle liquor.

Besides these, there can be several other causes of

contamination. But these differ from steel mill to steel mill, so people must investigate their particular sources of contamination for removing.

### 3. Waste Pickle Liquor Purification Process

Though Si is the most influential impurity in the magnetic properties of Mn-Zn ferrites, it is also very difficult to remove since it exists at nanometer size colloidal SiO<sub>2</sub> in the waste pickle liquor. Several methods have been developed for removing it such as filtration [1], adsorption [2], re-crystallization [3], and so on.

We developed a novel process based on the coprecipitation method which can remove SiO<sub>2</sub> and some other harmful impurities such as P simultaneously.

Colloidal SiO<sub>2</sub> in the waste pickle liquor tends to carry negative charges with the raising of pH, which is achieved by the dissolution of iron scrap. On the other hand Al ion, having positive charges, shows a sig-

Table 1. Source ratio of Si and Ca in the waste pickle liquor

Sources	Si	Ca
Industrial water	21%	91%
Dissolved scale compositions	73%	-
Others	6%	9%

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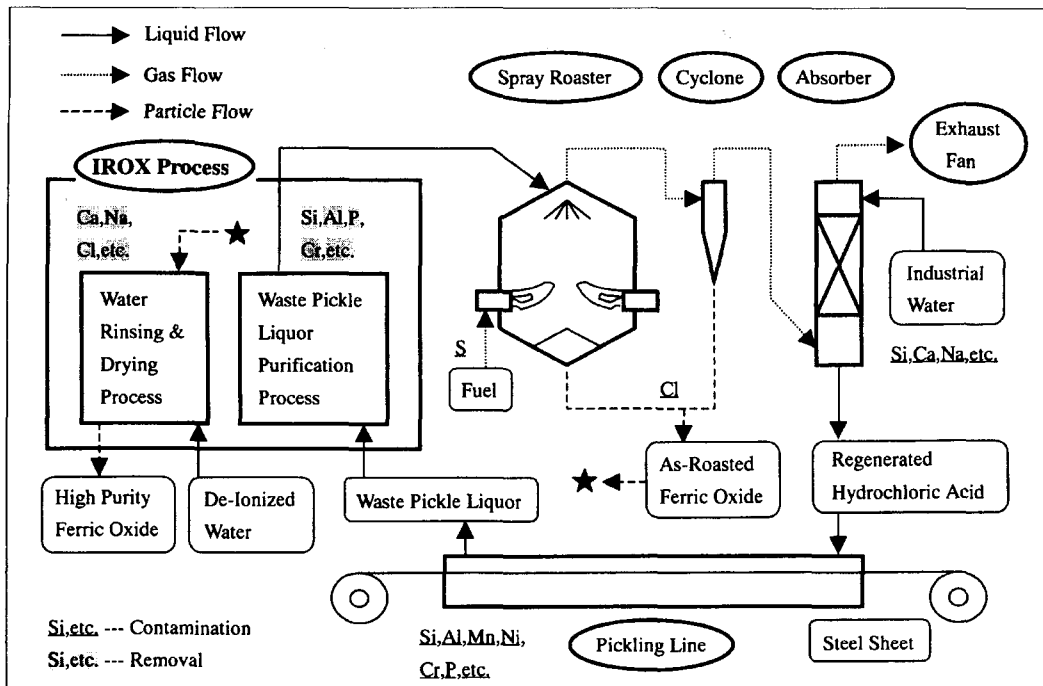


Fig. 1. Flow chart of high purity ferric oxide production process.

nificant change in solubility with the raising of pH. Therefore, if Al ion is added to the solution and the pH is raised up to 3~6 by adding alkali, then Al ion attracts  $\text{SiO}_2$  colloid and precipitates as insoluble  $\text{Al}(\text{OH})_3$ . This procedure is illustrated in Fig. 2.

As for other impurities, the elements which form insoluble hydroxide or oxide with the raising of pH

can be removed in the same way.

#### 4. Water Rinsing Process

Alkali metal and alkaline earth metal cannot be removed by this process from the waste pickle liquor because of their high solubility. In the IROX-NKK

Process stage	pH						Illustration	
	0	1	2	3	4	5		
Waste pickle liquor	●						<p><math>\text{SiO}_2^-</math>   <math>\text{SiO}_2^-</math></p>	$\text{SiO}_2$ colloid repulses each other due to surface charge
Fe scrap dissolving		●					<p><math>\text{Al}^+</math>   <math>\text{SiO}_2^-</math>   <math>\text{SiO}_2^-</math></p>	Al ion attracts $\text{SiO}_2$ colloid with opposite charge
$\text{AlCl}_3$ addition			●				<p><math>\text{Al}^+</math>   <math>\text{Al}(\text{OH})_3</math></p>	Al ion forms insoluble hydroxide with the raising of pH and precipitates together with $\text{SiO}_2$ colloid
$\text{NH}_4\text{OH}$ addition				●			<p><math>\text{Al}(\text{OH})_3</math>   <math>\text{SiO}_2</math></p>	Al ion forms insoluble hydroxide with the raising of pH and precipitates together with $\text{SiO}_2$ colloid
Co-precipitation					●		<p><math>\text{Al}(\text{OH})_3</math>   <math>\text{SiO}_2</math></p>	Al ion forms insoluble hydroxide with the raising of pH and precipitates together with $\text{SiO}_2$ colloid

Fig. 2. Illustration of waste pickle liquor purification process.

**Table 2.** Impurity level of several IROX-NKK's ferric oxide (wt%)

Brand	SiO <sub>2</sub>	Al	Mn	Ni	Cr	P	Ca	Na	Cl
HD (unpurified, unrinsed)	0.055	0.033	0.198	0.013	0.028	0.013	0.016	0.012	0.185
SM (purified, rinsed)	0.008	0.002	0.204	0.012	<0.001	<0.001	0.007	0.001	0.088
SEW (further purification)	0.003	0.001	0.201	0.008	<0.001	<0.001	0.002	<0.001	0.084

process, as roasted ferric oxide is rinsed by de-ionized water for removing them. Industrial water should not be used for rinsing because the colloidal SiO<sub>2</sub> in it will be adsorbed by the ferric oxide. This rinsing process also contributes to reduce Cl content in the ferric oxide.

### 5. Further Purification

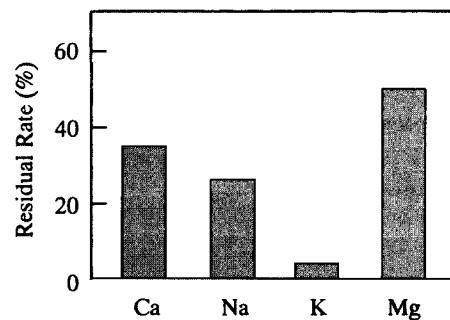
The effect of water rinsing is not perfect. Even if a large quantity of de-ionized water is used, a certain amount of alkali metal and alkaline earth metal still remain in ferric oxide.

Fig. 3. shows the residual rate of such impurities in ferric oxide after rinsing and drying.

It suggests that a portion of these impurities is trapped within the ferric oxide crystals during spary roasting.

For further purification, de-ionized water can be used as a replacement for the industrial water in the absorber because the major source of these impurities is the industrial water.

Table 2 shows the impurity level of several IROX-NKK's ferric oxide products to compare the effect of

**Fig. 3.** Water rinsing effect on impurities of ferric oxide.

each purification process.

SM is now widely used for low power loss Mn-Zn ferrite cores, and SEW is a recently developed product suitable for high permeability Mn-Zn ferrite cores.

### References

1. Japan. Patent 1408381.
2. Japan. Patent 1830908.
3. Y. Yamazaki and M. Matsue : Digests of ICF6, p. 1 (1992).