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A New Acid and Iron Recovery Process in Stainless Steel Annealing and Pickling Line*



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A new recovery process was developed for nitric-hydrofluoric acid waste liquor from the stainless steel annealing and pickling line (APL) at Chiba Works. Although the conventional neutralization treatment has drawbacks of generating a large amount of sludge and discharging nitrogen into public waters, the new process has advantages of overcoming these drawbacks and recovering acid and iron contents as well. The process principally consists of (1) the iron separation stage, (2) iron oxide formation stage, (3) nitric-hydrofluoric acid recovery stage and (4) ferrite formation stage. This process is realized in the recovery plant on an industrial scale of 24 m³/day. The plant is composed of mixer-settlers, crystallizers, rotary kilns, pulse columns and others.

The plant is in full operation with iron extraction percentage of 95% or more and recovery percentages of 95% or more for nitric acid and 70% or more for hydrofluoric acid.

1 Introduction

An annealing and pickling line (APL) for hot strip was constructed and commissioned in October 1982¹⁾ at Chiba Works as part of the streamlining program of the stainless steel manufacturing process. In constructing this APL, Kawasaki Steel gave high priority to environmental protection. Sludge generation and nitrogen discharge into public waters were reduced to a much greater extent than with the conventional neutralization treatment process through the introduction of a solvent extraction technique—a new treatment process for nitric-hydrofluoric acid waste liquor.

In the general method of pickling stainless steels in APL's, sulfuric acid is first used, followed by a mixed nitric-hydrofluoric acid. The pickling capacity decreases gradually as the amount of steel pickled increases, because free acids in the pickling liquor decrease and the concentration of dissolved metals increases. To ensure stable production, it is desirable to maintain constant concentration and composition of the pickling solution. The APL at Chiba Works is equipped with a pickling liquor circulation system, and the concentration and composition of the pickling solution are controlled by adding or discharging proper amounts of acids as required.

In treating the discharged sulfuric acid waste liquor, discharged metallic constituents (iron, chromium and nickel) are recovered as a composite oxide by the ferrite formation method applied to a concentrated ferrous salt solution, a newly introduced technique, and gypsum is obtained from sulfate.

In treating the nitric-hydrofluoric acid waste liquor, nitric-hydrofluoric acid and iron oxide are recovered by the solvent extraction method. This method will be the

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main theme of this paper. The raffinate after the recovery, containing chromium and nickel, is conducted to the above-mentioned ferrite formation stage where these metals are converted into a composite oxide.

As mentioned above, Kawasaki Steel successfully undertook the development of a new waste acid treatment technique characterized by high-efficiency nitric-hydrofluoric acid recovery by iron extraction. This epoch-making industrial process, as described below, is called the Kawasaki Steel Process.²⁾

2 History of Introduction of Solvent Extraction Technique

Nitric-hydrofluoric acid waste liquor has conventionally been treated by the lime neutralization method. However, the generation of a large amount of sludge and discharge of large amounts of nitrogen posed problems, and the development of techniques for recovering acids and metals from the waste liquor were desired.

For this reason, recovery techniques such as the evaporation method and ion exchange method have been examined. However, none of these methods has reached the stage of practical applicability. Studies were also made of the solvent extraction method, as embodied in "AX Process" in Europe^{3,4)}.

In Japan, a technique for recovering nitric acid and hydrofluoric acid by the solvent extraction method was for the first time put to commercial use at Nisshin Steel Co., Ltd.⁵⁾ Kawasaki Steel, to further develop this "Nisshin Process" while making the most of its advantages, gave attention to the principle⁶⁻⁹⁾ of high-efficiency hydrofluoric acid recovery by incorporating an iron separation stage upstream in the Nisshin Process. Kawasaki Steel then decided on the introduction of a process based on this principle.

Incidentally, the development of this process was carried out as a subject for development entrusted to Kawasaki Steel by the Research Development Corporation of Japan under the designation "Recovery technique for steel pickling waste liquor by iron extraction."

3 Acid Recovery Technique by Solvent Extraction Method

3.1 Outline of Solvent Extraction Method¹⁰⁾

The solvent extraction method is a separation technique utilizing the distribution of substances between two immiscible liquid phases (in general, the aqueous phase and the organic phase). This method consists of the following three steps:

- (1) Extraction—transferring the object constituent from the aqueous phase to the organic phase by action of an extractant,

- (2) Scrubbing—scrubbing impurities co-extracted or carried into the organic phase and removing them into the aqueous phase,
- (3) Back-extraction or stripping—transferring the object constituent from the organic phase to the aqueous phase.

The solvent extraction method, which has been developed since the 19th century as a technique in the field of analytical chemistry, is widely used today. Especially in the field of hydrometallurgy, this method has become indispensable to the processes of extraction, separation, enrichment, and recovery of metals ranging from common to rare metals. In the steel industry as well, the solvent extraction method has been adopted mainly for the recovery treatment of steel pickling waste liquor, as will be described later.

An organic solvent is principally composed of an extractant and a diluent. Among various types of extractants, those used in the Kawasaki Steel process are di-2-ethylhexyl phosphoric acid (D2EHPA), classified among the alkyl phosphoric acids, and tributyl phosphate (TBP), classified among the phosphoric acid esters.

3.2 Utilization of Solvent Extraction Method in Steel Industry

Techniques used in the steel industry for steel pickling waste liquor recovery by the solvent extraction method are given in Table 1. The first application of this method in the steel industry was the Republic Steel process¹¹⁾ in 1962. However, there have been no reports that this process was used commercially. The first full-scale application of the solvent extraction method was the AX process (Sweden) in 1973. In Japan, Nisshin Steel Co., Ltd. completed the Nisshin process in 1978 by improving the AX process.

AX process and Nisshin process have the following common advantages:

- (1) The nitric acid recovery percentage is high and the amount of nitrogen discharged is small.
- (2) The recovered acids do not contain metals.
- (3) Energy consumption is low.

The AX process involved the problem of sludge increase caused by gypsum generation resulting from the addition of sulfuric acid to convert metal nitrates and fluorides into HNO₃ and HF. In the Nisshin process, however, this problem is solved by using hydrochloric acid instead of sulfuric acid. Furthermore, the Nisshin process has the following features:

- (1) Nitric acid and nitric-hydrofluoric acid are fractionally recovered by utilizing the different extraction distribution ratios between HNO₃ and HF relative to tributyl phosphate.
- (2) The sludge formed contains Fe, Cr, and Ni and can be reused as a raw material for steelmaking.

Table 1 Application of solvent extraction in steel industry

	Republic Steel Process	AX Process	Nisshin Process	Kawasaki Steel Process
Beginning	1962	October 1973	April 1976	September 1981
Location	[Republic Steel (U.S.A.)]	Stora Kopparberg, Söderfors Works (Sweden)	Nisshin Steel, Shunan Works (Japan)	Kawasaki Steel, Chiba Works (Japan)
Process	Oxidation of Fe ²⁺ →Fe ³⁺ complexing with SCN ⁻ →Extraction of Fe ³⁺ complex →Stripping by NH ₃	Addition of H ₂ SO ₄ →Extraction of free HNO ₃ and HF →Stripping by water	Addition of HCl →Extraction of free HNO ₃ and HF →Stripping by HNO ₃ or water	A: Fe ³⁺ extraction →Fe ³⁺ stripping by NH ₄ HF ₂ solution →Heating of (NH ₄) ₃ FeF ₆ in air B: Addition of HCl →Acid extraction →Acid stripping by water
Solvent	25% TBP+75%Kerosene	75% TBP+25%Kerosene	75%TBP+25%Aromatic hydrocarbons	A: 30%D2EHPA +70%n-paraffin B: 70% TBP+30%n-paraffin
Recovered materials and recovery percentages	H ₂ SO ₄ and Fe ₃ O ₄	HNO ₃ -HF	HNO ₃ -HF and HNO ₃ HNO ₃ : 94%, HF: 16%	HNO ₃ -HF and Fe ₂ O ₃ HNO ₃ : 95% or more HF: 70% or more Fe: 95% or more
Sludge generation*	—	100	79	11

* Percentage to sludge generation by neutralization process of the same treatment capacity

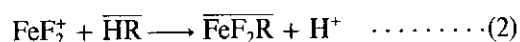
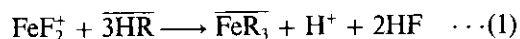
Incidentally, since Fe³⁺ in the waste acid forms complex ions with F⁻, it was expected that the HF recovery rate can be further improved if these complex ions are decomposed.

3.3 Acid Recovery Technique by Iron Extraction (Kawasaki Steel Process)

The flow sheet of the Kawasaki Steel process is shown in Fig. 1. The principal stages of this process are iron separation, iron oxide formation, nitric-hydrofluoric acid recovery, and ferrite formation.

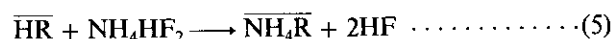
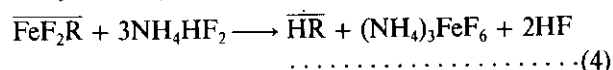
3.3.1 Iron separation stage

Fe³⁺ in the nitric-hydrofluoric acid waste liquor (mainly in the ionic forms FeF₂⁺ and FeF₂²⁺) is extracted in the Fe extraction step through ion exchange reactions with solvent A (30% D2EHPA + 70% n-paraffin). The extractant D2EHPA (HR in the following equations) selectively extracts only Fe³⁺ in the strongly acidic region. Examples of reaction formulas are given as follows:



where the overbars denote species in the organic phase. Fe³⁺ extracted in the organic phase reacts with a fluo-

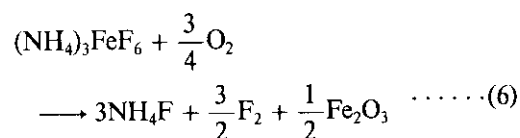
ride series stripping solution (NH₄HF₂ aqueous solution) in the Fe stripping step. As a result, this Fe³⁺ is stripped as a ferric ammonium fluoride complex (NH₄)₃FeF₆ in the aqueous phase and precipitates as crystals (see Photo 1).



Part of the extractant after Fe stripping takes an ammonium form (NH₄R) due to such reactions as given by formula (5). As a result, solvent A is converted into a hydrogen form (HR) due to contact with the aqueous phase containing hydrochloric acid. The solvent is then is reused for Fe extraction.

3.3.2 Iron oxide formation stage

The ferric complex crystal becomes an iron oxide (α-Fe₂O₃) by heating and decomposition in the air or in a gas containing steam.



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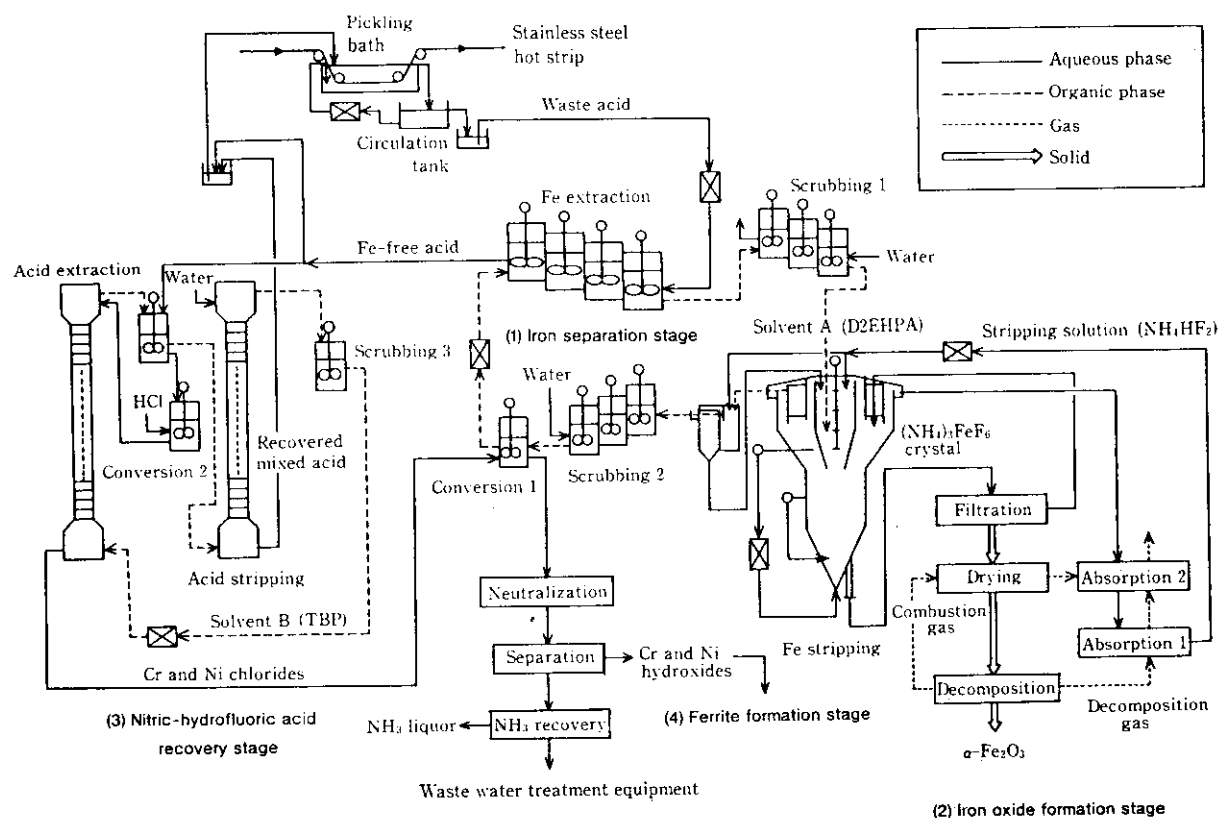
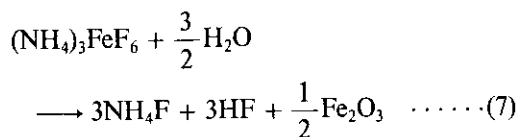
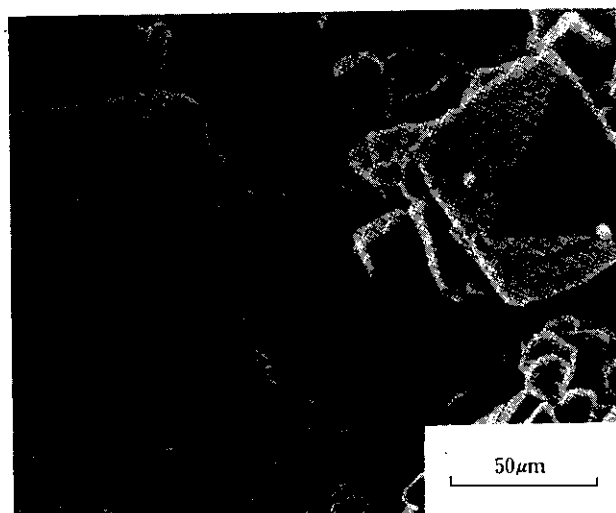


Fig. 1 Flow sheet of Kawasaki Steel Process

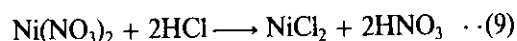
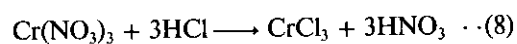


To prevent an increase in the Cr and Ni concentra-

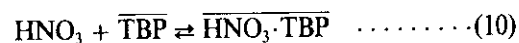
tions of the pickling solution, part of the waste acid (Fe-free acid) after Fe extraction is conducted to the nitric-hydrofluoric acid recovery stage, and the remaining part is reused as recovered Fe-free acid in the APL.

3.3.3 Nitric-hydrofluoric acid recovery stage

By adding HCl, the metal nitrates in the Fe-free acid are converted into chlorides, and HNO_3 is set free.



Next, nitric-hydrofluoric acid is extracted using solvent B (70% TBP + 30% n-paraffin).

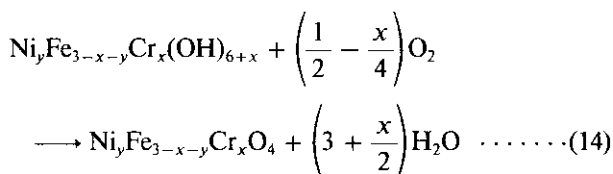
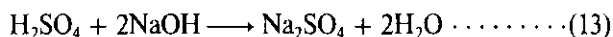
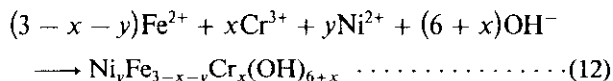


The nitric-hydrofluoric acid extracted into the organic phase is stripped by water and reused as recovered mixed acid in the APL.

3.3.4 Ferrite formation stage

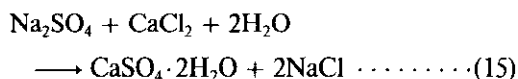
Since the raffinate after nitric-hydrofluoric acid extraction contains chlorides of Cr, Ni, etc., it is conveyed to the waste water treatment equipment after

these chlorides are neutralized and separated. The metal hydroxide slurry obtained is mixed with the sulfuric acid waste liquor and is then subjected to ferrite formation treatment, as a result of which it becomes a composite metal oxide and can be reused. Examples of reaction formulas are shown below:



where $0 \leq x \leq 2$, $0 \leq y \leq 1$.

Since the filtrate after the reaction contains SO_4^{2-} , CaCl_2 is added to cause gypsum to form. The filtrate after gypsum separation is conveyed to the waste water treatment equipment.



4 Development of the Kawasaki Steel Process

4.1 Progress of Development

The progress of development of the Kawasaki Steel process is shown in Fig. 2. Fundamental experiments were started in September 1981 following the decision to introduce a solvent extraction technique. The recovery plant was designed based on the results of the experiments and information on the solvent extraction method obtained from enterprises where the method was already in use. The plant was completed in September 1982 (see Photo 2).

The plant was started up in October 1982, and equipment and process problems were examined during operation. The iron separation stage (especially the Fe stripping step) and the iron oxide formation stage posed

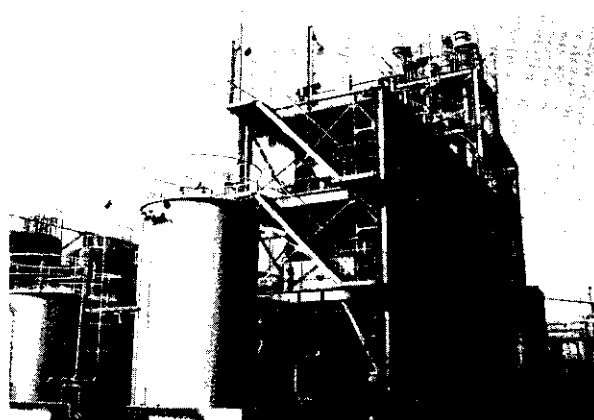


Photo 2 General view of acid recovery plant

major problems in the course of development. However, these problems were solved by modifying equipment, improving the process, and establishing operating techniques. As a consequence, this recovery plant has since been operating smoothly according to specifications.

4.2 Fundamental Examination of Process

4.2.1 Fe extraction step

(1) Composition of Solvent A and Fe Extraction Equilibria

As a result of analysis, it was found that solvent A contains mono-2-ethylhexyl phosphoric acid (M2EHPA) in an amount corresponding to about 1/6 the molar concentration of D2EHPA.

Figure 3 shows Fe extraction equilibrium curves for an Fe^{3+} -containing nitric-hydrofluoric acid aqueous solution with different HF concentrations and solvent A (30% D2EHPA + 70% n-paraffin). This figure shows also the equilibrium curve (indicated by broken line M) for a solvent containing D2EHPA and M2EHPA of almost equal molarity as extractants. The Fe extraction percentage increases markedly when M2EHPA is added.¹²⁾ However, problems occur during solvent scrubbing, as will be described later.

Year	1981	1982	1983	1984
(1) Fundamental investigation				
(2) Plant construction				
(3) Plant operation				
(a) Test run				
(b) Modification and improvement				
(c) Overall plant operation				

Fig. 2 Progress in development of Kawasaki Steel Process

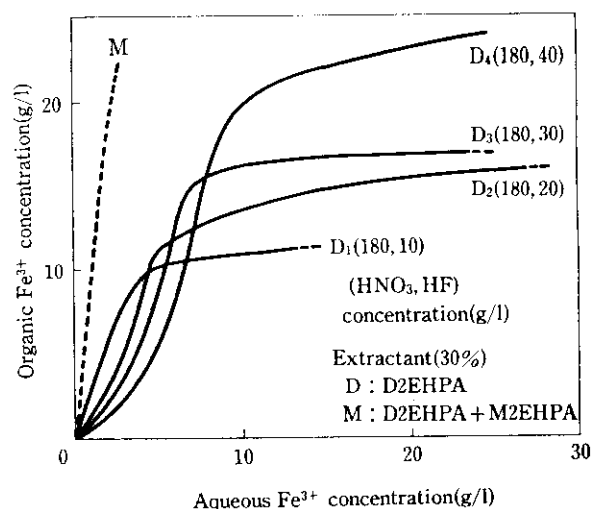


Fig. 3 Fe extraction equilibria in HNO₃-HF solution

Furthermore, it was found that the F/Fe molar ratio in the solvent after extraction is about 1.0 for a waste acid of the standard composition shown in Sec. 4.3, and in consequence, the upper limit of the HF recovery percentage is about 75%.

(2) Continuous Experiments Using Extraction Apparatus

A continuous experiment in the iron separation stage was conducted three times using the equipment of Solex Research Corporation of Japan. The waste acid treatment capacity of this equipment is about 1 to 3 l/h; its Fe extraction portion comprises a counter-current three-stage mixer-settler. The experimental conditions and results are shown in Table 2. The Fe concentration of the recovered Fe-free acid is efficiently reduced as the residence time of two liquid phases in the mixer portion increases.

(3) Solvent Scrubbing After Fe Extraction

To remove nitric-hydrofluoric acid solution included as liquid drops containing Cr and Ni, it is necessary to scrub solvent A containing extracted Fe³⁺. However, the fact that solvent A may become highly viscous or solidify if scrubbed with water is a problem. This tendency becomes especially serious as

the level of M2EHPA in the extractant increases. This phenomenon was avoided by scrubbing solvent A with aqueous solutions of about 10 to 100 g/l HNO₃, HF, HNO₃ + Hf, NH₄HF₂, etc.¹³⁾

4.2.2 Fe stripping step

(1) Solubility Curves of Ferric Complex

The Fe³⁺ stripping reaction given in Formulas (3) and (4) causes (NH₄)₃FeF₆ crystals to precipitate. At the same time, the NH₄HF₂ concentration of the stripping solution decreases and the HF concentration increases. As this change in the concentration and composition of the stripping solution was found to have a remarkable effect on the solubility of (NH₄)₃FeF₆, as shown in Fig. 4, it was decided to examine optimum concentration and composition conditions of the stripping solution using actual equipment.

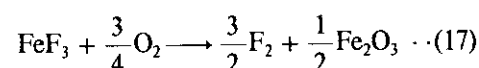
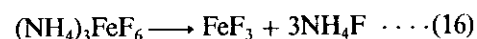
(2) Deterioration of Organic Solvent by Fe Stripping

To promote the Fe³⁺ stripping reaction and ensure the growth of the ferric complex crystal, solvent A is warmed by mixing it with a heated stripping solution. However, if the solvent temperature exceeds 40°C, the Fe extraction percentage will decrease sharply when the solvent is next used in Fe extraction¹⁴⁾.

4.2.3 Iron oxide formation stage

(1) Thermal Decomposition of Crystal

The results of thermal analysis of (NH₄)₃FeF₆ are shown in Fig. 5. From the TGA (thermo-gravimetric analysis) and DTA (differential thermal analysis) curves, it is apparent that iron oxide formation as expressed in Formula (6) takes place in two steps, through the following reactions:



Both are endothermic reactions and the entire reaction is completed at about 500°C.

(2) Reduction of P and F in Iron Oxide

Table 2 Continuous experiments in iron separation stage

No.	Date	Composition of waste acid (g/l)		Composition of Fe-free acid (g/l)		Flow rate (l/h)			τ^* (min)	O/A**)	
		Fe ³⁺	HF	Fe ³⁺	HF	Waste acid	Solvent A	Stripping solution		Extraction	Stripping
Run 1	October 14 & 15, 1981	36.04	30.0	1.65	—	3.0	5.6	22	7.4	1.9	1/3.92
Run 2	November 5 & 6, 1981	38.6	34.2	0.44	22.1	1.2	2.5	—	17.2	2.1	—
Run 3	December 2-4, 1981	27.98	40.05	1.11	29.48	2.05	4.56	15.5	9.64	2.22	1/3.40

* Residence time in one-stage mixer part

** Flow ratio of organic phase to aqueous phase

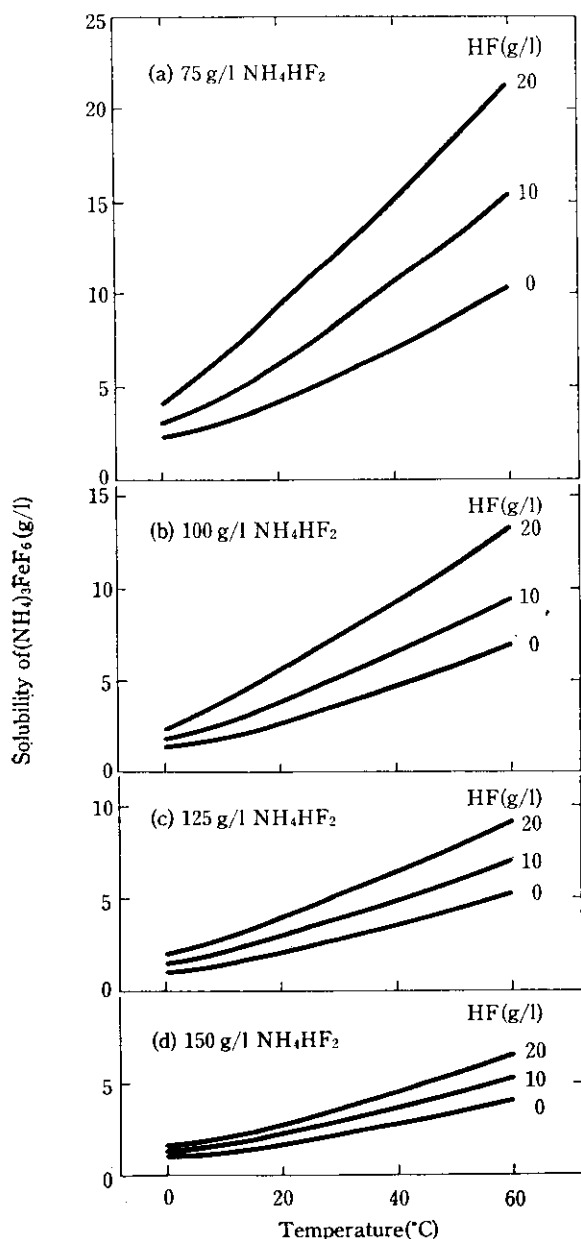


Fig. 4 Solubility curves of $(\text{NH}_4)_3\text{FeF}_6$ for NH_4HF_2 -HF solution

P, originating in the solvent A extractant and adhering to the crystal, and F, originating in undecomposed FeF_3 , became problems as impurities in the formed iron oxide. It was possible to remove P by washing¹⁵⁾ crystals with n-paraffin before heating. Although the amount of F was reduced by raising the heating temperature to above 650°C , more practical heating conditions were examined using an actual kiln.

(3) Purity of Iron Oxide

Examples of analysis of the formed iron oxide are shown in Table 3. In sample 2, an Fe_2O_3 purity of

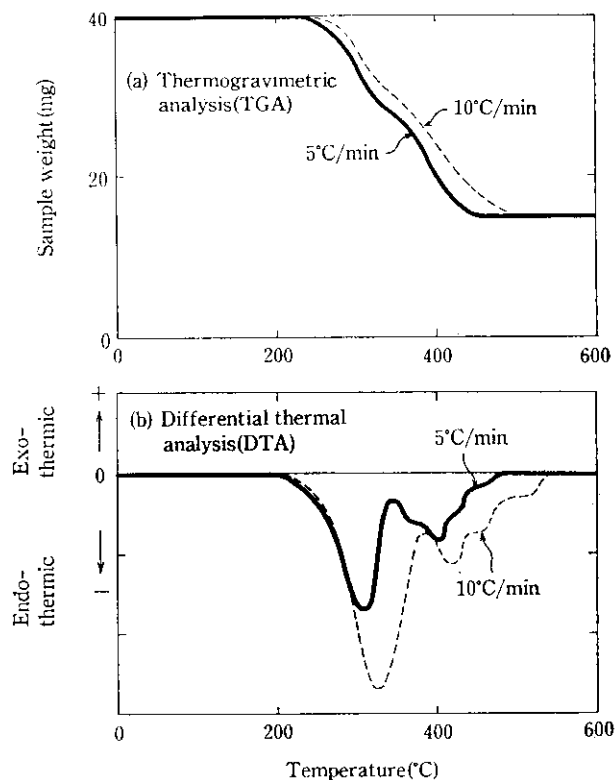


Fig. 5 Thermal analysis curves of $(\text{NH}_4)_3\text{FeF}_6$

Table 3 Chemical composition of iron oxide obtained at laboratory

Sample	Content of element (%)					Purity as Fe_2O_3 (%)
	Fe	Cr	Ni	P	F	
Sample 1	70.0	—	—	0.03	0.18	99.6
Sample 2	70.0	0.020	<0.001	<0.01	<0.02	99.9

99.9% was achieved.

4.3 Recovery Plant

4.3.1 Waste acid composition and design specifications

In designing the recovery plant, it was necessary to take the following points into consideration:

- (1) Variations in the amount and the concentration and composition of the waste acid according to the steel grade pickled
- (2) Effects of such factors as the concentration and composition of waste acid, flow ratio of the organic phase to the aqueous phase (O/A), residence time of two liquid phases, and number of extraction stages on the Fe extraction percentage and HNO_3 and HF recovery percentages

Table 4 Plant specification

(a) Standard composition of waste acid

Constituent	Concentration (g/l)
Acid	HNO ₃ 180-200
	HF 40-45
Metal	Fe 28-30 (max. 35)
	Cr 10-15
	Ni 5-10

(b) Specifications

Stage	Waste liquor	Treatment capacity	Extraction or recovery percentage
Iron separation	Waste acid	1.0 m ³ /h (24 m ³ /day)	Fe extraction: 95% or more
Nitric-hydrofluoric acid recovery	Fe-free acid	0.3 m ³ /h (7.2 m ³ /day)	HNO ₃ recovery: 95% or more HF recovery: 70% or more

- (3) Deposition of FeF₃ crystals due to increases in the concentrations of Fe³⁺ and HF
- (4) Stationary values of Cr and Ni concentrations during the reuse of the recovered Fe-free acid in the pickling process of the APL

As a result of an examination of the above-mentioned points, the standard composition of the waste acid supplied to the recovery plant and the design specifications of the plant were determined as shown in Table 4.

4.3.2 Outline of the plant

The iron separation stage consists of mixer-settlers for Fe extraction and scrubbing (steps 1 and 2), crystallizers for Fe stripping, and heat exchangers for warming

and/or cooling the waste acid, stripping solution, and solvent A. A top view of the principal equipment of the plant is shown in Photo 3. The Fe extraction mixer-settler is of a counter-current, four-stage box type.

The iron oxide formation stage consists of drying and decomposition kilns, and fluorine series decomposition gas absorption columns.

The nitric-hydrofluoric acid recovery stage is composed of pulse columns for acid extraction and stripping.

4.4 Development of Stages

4.4.1 Iron separation stage

(1) Operation in Fe Extraction Step

An examination was made of the treatment capacity of the Fe extraction apparatus for waste acid of standard composition. Figure 6 shows Fe extraction data obtained with a fixed O/A ratio of 2.0 and amounts of treated waste acid varying between 0.5 and 1.3 m³/h. Figure 7 shows Fe extraction data with the amount of treated waste acid fixed at 1.0 m³/h and O/A varied between 1.5 and 2.0. It was found from these results that Fe extraction percentages of 95% or more can be achieved even with waste acid treatment rates of up to 1.3 m³/h if O/A is held between 1.8 and 2.0.

(2) Modification of Fe Stripping Apparatus

When Fe stripping was carried out using the conventional apparatus shown in Fig. 8(a), various phenomena occurred to impede the continuous operation of the apparatus, for example, adhesion of deposited crystals on the inner wall surface, accumulation and agglomeration of deposited crystals in the lower section of the apparatus, and inclusion of solvent A into the crystal slurry.

To solve the above-mentioned problems, the apparatus was modified,^{16,17)} especially in the following three areas:

- Installation of a stripping solution forced circulation zone
- Shortening of the downpipe

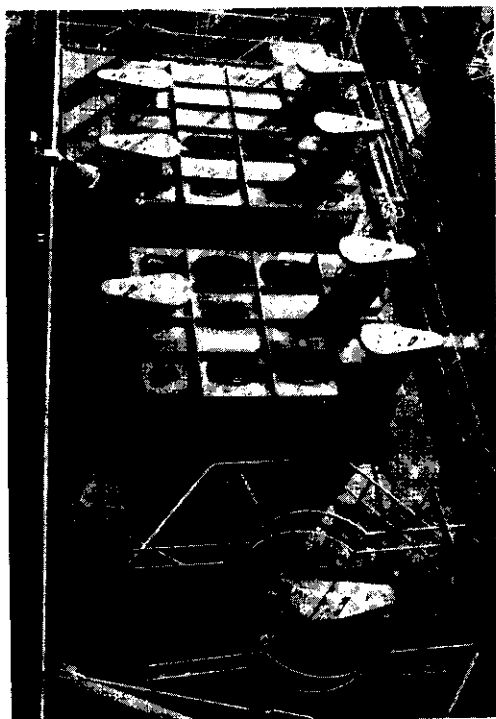


Photo 3 Fe extraction and scrubbing mixer-settlers and crystallizer viewed from above

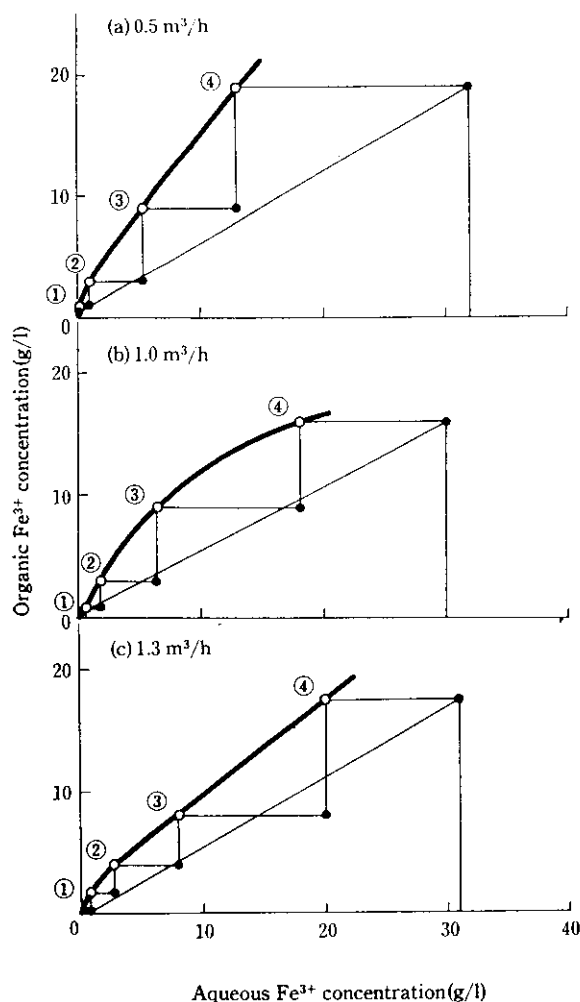


Fig. 6 Fe extraction curves for varied treating rate ($O/A = 2.0$) (○: Stage number of mixer-settler)

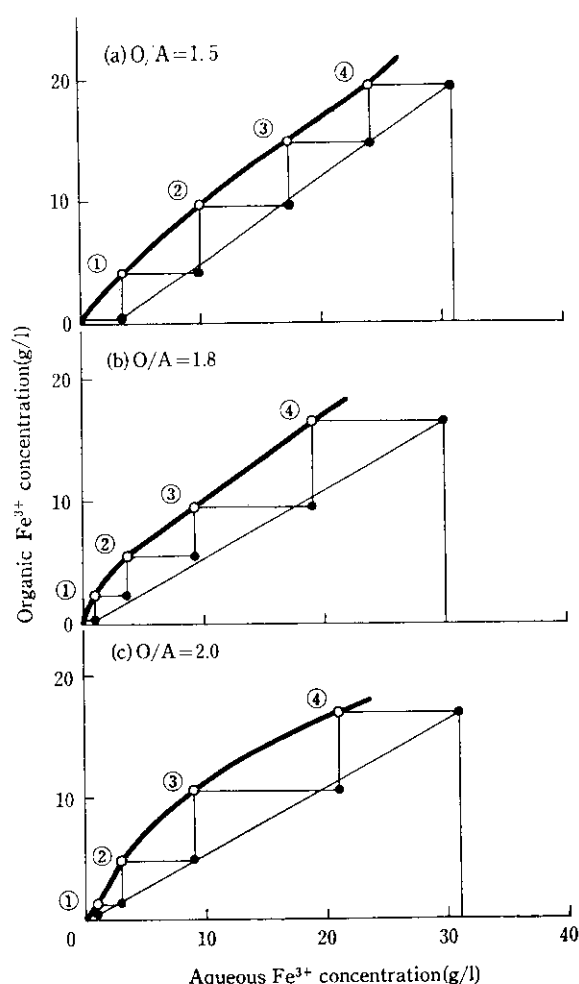


Fig. 7 Fe extraction curve for varied O/A (Treating rate $1.0 \text{ m}^3/\text{h}$) (○: Stage number of mixer-settler)

(c) Change of the position of the outlet for cooled stripping solution

These modifications virtually eliminated the above-mentioned problems.

(3) Determination of Fe Stripping Conditions

Based on the results of fundamental studies, Fe stripping conditions,^{18,19)} aimed at preventing the undesirable deposition of crystals in the crystallizer and neighboring piping and equipment, preventing the deterioration of solvent A, and maintaining constant crystallization conditions unaffected by air temperature, were determined as follows:

(a) Optimum Conditions for Concentration and Composition of Stripping Solution

The concentration of the stripping solution supplied to the crystallizer is controlled so that the NH_4HF_2 concentration of the stripping solution discharged from the apparatus is 85 g/l or more, while the HF concentration is 10 g/l or less.

(b) Temperature Range of Stripping Solution and solvent A

- Solvent A supplied to crystallizer: 20 to 25°C
- Mixed solvent A and stripping solution: 40°C or below
- Stripping solution in the cooling zone: 15 to 20°C

(c) Supply Points of Chemicals for Control of Concentration and composition of Stripping Solution

- NH_4HF_2 solution: Lower section of crystallizer
- Discharged stripping solution with absorbed fluorine series crystal decomposition gas: Mixing zone of crystallizer
- NH_3 gas: Receiving tank for crystal slurry discharged from crystallizer
- Filtrate after crystal separation: Stripping solution settling zone of crystallizer

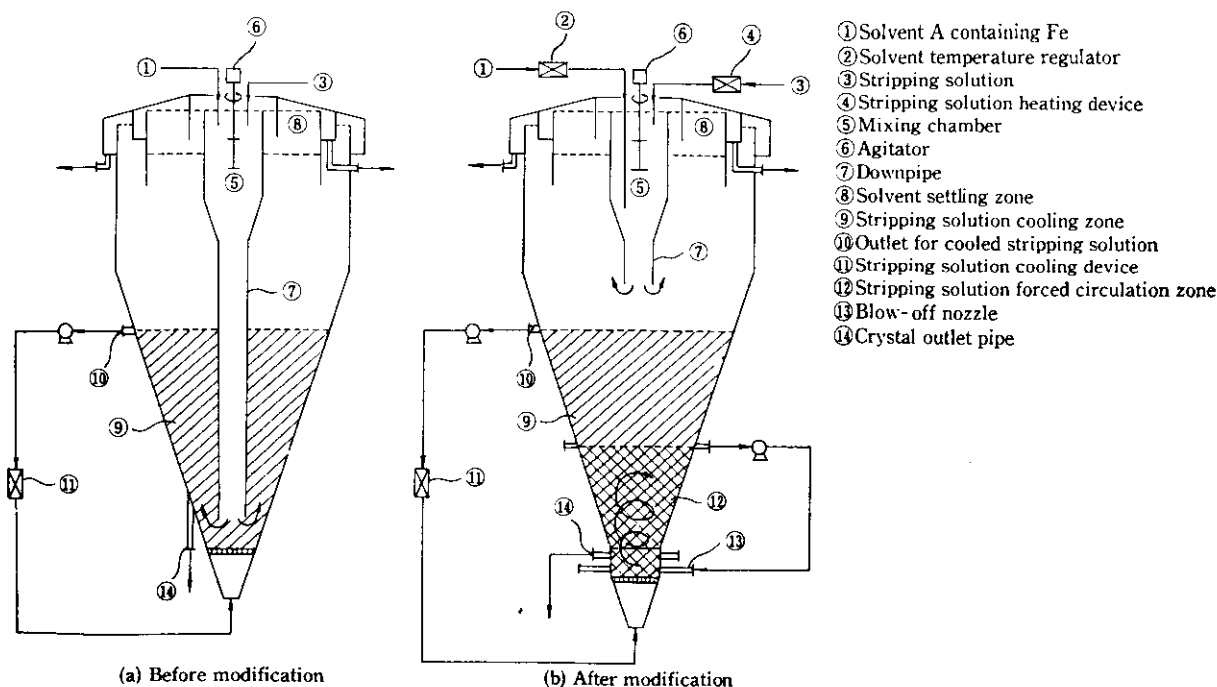


Fig. 8 Schematic view of Fe stripping crystallizer

4.4.2 Iron oxide formation stage

In the initial stage of development, the rate of ferric complex crystal decomposition was low, and the Fe_2O_3 purity of the iron oxide formed was about 70 to 80%. Therefore, experiments were conducted using a test kiln, and partial modification of the decomposition kiln and changes in heating conditions, such as raising the temperature, were implemented.

As a result, the purity of the iron oxide which formed increased to 95 to 98%, as shown in Table 5. Furthermore, because the amount of crystal decomposition increased, a greater amount of fluorine series decomposition product came to be absorbed in the stripping solution and reused, and thus the operation of the Fe stripping step became stable.

Table 5 Chemical composition of iron oxide manufactured

Sample	Content of element (%)					Purity as Fe_2O_3 (%)
	Fe	Cr	Ni	P	F	
Test kiln sample	68.9	0.034	0.019	0.02	2.46	95.1
Product 1	67.1	0.04	0.01	—	2.47	95.1
Product 2	68.3	0.04	0.02	—	1.42	97.2
Product 3	68.2	0.05	0.01	—	0.91	98.2

4.4.3 Nitric-hydrofluoric acid recovery stage

The recovery plant has been in continuous operation since January 1984. During this period, the performance of the nitric-hydrofluoric acid recovery equipment has also been confirmed. As shown in Table 6, the design specifications of an HNO_3 recovery percentage of 95% or more and an HF recovery percentage of 70% or more are being achieved.

Table 6 Recovery percentage of acids

Stage	Treating rate (m^3/h)	Recovery		
		Yield (m^3/h)	Recovery (%)	
			HNO_3	HF
Iron separation	1.00	0.70	98.5	75.3
Nitric-hydrofluoric acid recovery	0.30	0.35	95.7	79.5
Total	(1.00)	1.05	97.2	70.7

5 Conclusions

In the treatment of nitric-hydrofluoric acid waste liquor, a new method of acid recovery to replace the neutralization method has long been desired. The realization of this dream is now possible with utilization of the solvent extraction method.

However, the fluorine ions in the nitric-hydrofluoric

acid waste liquor cannot be extracted as an acid because they combine with ferric ions to form complexes. Therefore, the hydrofluoric acid recovery percentage has been low. To improve this situation, a solvent extraction method for separating iron content was incorporated in this new process, making possible a striking improvement in the hydrofluoric acid recovery percentage. Iron extraction percentages of 95% or more, nitric acid recovery percentages of 95% or more, and hydrofluoric acid recovery percentages of 70% or more are attained in this new process.

As mentioned above, the separation and recovery of the iron content of waste acids in the new process is of great significance. Furthermore, it is expected that the practical application of this technique will, in the future, give impetus to the recovery of various metals by the solvent extraction method. Moreover, it was also possible to further develop the Kawasaki Steel process into an overall recovery treatment technique for stainless steel pickling waste liquor, by combining the above-mentioned solvent extraction technique with a ferrite formation treatment technique for sulfuric acid waste liquor. This was especially important because it meant that a new waste acid treatment technique involving effective utilization of resources as well as environmental protection in stainless steel production in an APL was realized in this process.

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