Treatment of Waste Water Containing Vanadium and Chromium by a Two-Fractional Precipitation Process

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ABSTRACT

In this paper , a two—step fractional precipitation process for the treatment of waste water containing vanaduim and chromium is presented. An annual capacity of waste water treated can reach 100,000 tons with the existing equipment in Emei Ferroalloys Co. The contents of V and Cr after treatment conforms completely with the discharge standard stipulated by the State. Precipitates contain enriched V and Cr which can be recovered and used again. Recovery amounts to 87% and 85% respectively without secondary pollution.

1. Introduction

Large amount of acidic waste water containing 40-120mg/l Cr and 60-80mg/l V has been produced during the hydrometallurgical extraction of V from V slag . In order that this kind of waste water can reach the discharge standard so as not to pollute the environment and that metallic values can be recovered, various methods such as ion exchange, ferrous sulfate , SO_2 and iron oxide treatment have been used in various plants.

Originally the method of ion exchange was used to treat the waste water containing V and Cr in Emei company. Despite the fact that V in waste water can be recovered using this method, the dried residue of high concentration Cr containing solution co-produced was completely of no use and was just heaped up, causing a secondary pollution. In 1989, based on the comparison and analysis of various methods of treatment and the actual condition of production, a chemical method for separating and enriching V and Cr in waste water was under study to recover and use V and Cr respectively and discharge clean water simultaneously.

It took 3 years to conduct research and development, install equipment and carry out pilot plant production. In 1992 the process was put into operation. In the same year, 60,000 tons of waste water were treated with good results obtained. Since then, 100,000 tons of waste water have been treated annually. The recovered V-containing materials are completely returned to rotary kiln for oxidizing roasting. Cr containing materials were blended with Cr ore fines, sintered and fed into electric submerged arc furnace for smelting to ferrochromium. In 1996, the process was checked and accepted by the State Department of Environmental Protection. Good social and economical benefits have been achieved.

2. Sources and characteristics of waste water

2. 1 Technological flow process of V extraction from V slag and waste water production is shown in Fig. 1

2. 2 The form in which V and Cr exist in waste water

The highest values state of V is + 5. Since pentavalent V has a relatively large elecrostatic charge/radius ratio, simple V^{+5} ions do not exit in water solution; instead, V ions mainly exist in the form of oxy-acid radicals, such as VO_3, VO_4^{3-},etc. With the rising of acidity of solution, poly-vanadate ions with various degrees of polymerization are also capable of existence.

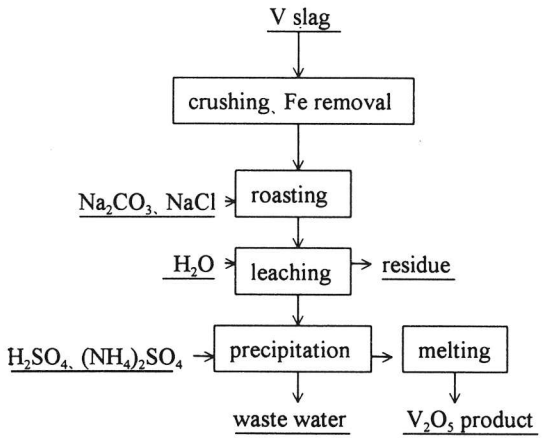

Fig.1 Flow process diagram of V_2O_5 and waste water

Cr mainly exists in the form of $Cr_2O_7^{2-}$ ions . The following equilibruim takes place in the solution between pH=2-6[1].

$$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2HCrO_4^-$$

2. 3 Composition of waste water sample

For analytical data of waste water sample, see Table 1.

3. Basic principles of waste water treatment by two step fractional precipitation

In weak acidic solution, Fe^{3+} and VO_3^-, VO_4^{3-} combine to form $Fe(VO_3)$ precipitate.
The reaction is as follows:

$$3VO_3^- + Fe^{3+} = Fe(VO_3)_3 \downarrow \quad (1)$$
$$3VO_4^{3-} + Fe^{3+} + 6H^+ = Fe(VO_3)_3 \downarrow + 3H_2O \quad (2)$$

The above reaction is effective for separating V from low-concentration V-containing solution. At the moment, Cr does not take part in any reaction and still remains in the solution. The $Fe(VO_3)_3$ precipitate can be separated by filtration from the upper layer of solution containing Cr.
The solution containing Cr after separation is added with sulfite to reduce hexavalent Cr in $Cr_2O_7^{2-}$ or CrO_4^{2-} to Cr^{+3}. The reaction is as follows [2]

$$Cr_2O_7^{2-} + 3HSO_3^- + 5H^+ = 3SO_4^{2-} + 2Cr^{3+} + 4H_2O \quad (3)$$
$$2CrO_4^{2-} + 3HSO_3^- + 7H^+ = 3SO_4^{2-} + 2Cr^{3+} + 5H_2O \quad (4)$$

Then alkali is added; the following reaction takes place:

$$Cr^{3+} + 3OH^- = 3Cr(OH)_3 \downarrow \quad (5)$$

Thus, V is separated first, and then Cr is reduced and precipitated, thereby separation and recovery of V and Cr being attained.

4. Experimental

4. 1 Experiments on separation of V and Cr in waste water

Firstly V was separated from waste water. Waste water was sampled from production site. Experiments of 200ml, 1000ml, 5000ml of waste water in glass beakers were carried out respectively. Ferric salt was used as precipitating agent with pH of waste water adjusted to 5 by NaOH solution. After standing for 5 minutes, the ferric vanadate formed rapidly, flocculated and settled. The results are shown in Table 2.
500 ml of the upper layer solution containg Cr was then added with sulfite under acidic condition. NaOH solution was added to adjust pH to 6-9. After standing for 5 minutes, chromic hydroxide rapidly flocculated and precipitated. The result is shown in Table 3:
On referring to Table 3, it will be noted that it is completely feasible to remove V and Cr in waste water by controlling the use of reagent and pH.

4. 2 Determination of the velocity of natural settling of precipitates containing V and Cr.

Since $Fe(VO_3)_3$ and $Cr(OH)_3$ precipitates are non-cryatalline, their velocities of natural settling will be extremely slow and bring about great difficulties to industrial production.
Therefore, the velocities were determined under different pH conditions and comparative tests on the effects of addition of flocculants were carried out, as

shown in Table 4.

As shown by the data in table 4, settling velocity of V precipitate varies with pH, being smaller at low pH, and becomes larger with the addition of flocculants. Nevertheless, the variations are not so remarkable. On the contrary, the settling velocity of Cr precipitate will increase by more than 400% with the addition of flocculant at the same pH.

Table 1 Analytical data of waste water sampled from the drain in the plant (unit:mg/l)

V	Cr	Fe	Si	Ca	Mg	Mn	P	Na_2SO_4	S	NH_3-N	pH	Oil	Smell	Color
60-80	40-120	2-5	100-200	65-220	30-120	30-50	0.045-0.066	40000-70000	70-100	930-1200	2.5-3	no	peculiar	yellow

. Discharged water should contain V<1.0mg/l and Cr<0.5mg/l, pH 6-9 according to GB 8978-1996. It is thus evident that the waste water from extraction should be treated.

Table 2 Experimental data on separation of V and Cr

Technical condition			Before treatment				After treatment				
Fe^{3+} (g)	NaOH (g)	Temp (℃)	Vol of solution(ml)	V (mg/l)	Cr (mg/l)	pH	Vol. of solution (ml)	V (ml)	Cr (ml)	pH	Color
1.0	0.7	25	200	60.8	126	2-3	200	0	114	acidic	yellow
0.8	0.7	25	200	60.8	126	2-3	200	0	110	acidic	yellow
0.6	0.7	25	200	60.8	126	2-3	200	0.7	100	acidic	yellow
0.4	0.7	25	200	60.8	126	2-3	200	0.8	118	acidic	yellow
0.2	0.7	25	200	60.8	126	2-3	200	1.1	110	acidic	yellow
5.0	3.0	25	1000	60.8	126	2-3	1000	0	105	acidic	yellow
4.0	3.0	25	1000	60.8	126	2-3	1000	0	112	acidic	yellow
3.0	3.0	25	1000	60.8	126	2-3	1000	0	111	acidic	yellow
2.0	3.0	25	1000	60.8	126	2-3	1000	0	115	acidic	yellow
2.5	1.5	25	5000	60.8	126	2-3	5000	0.5	105	acidic	yellow

Table 3 Data on Cr removal

Technical condition			Before treatment				After treatment				
SO_3^{2-} (g)	NaOH (g)	Temp (℃)	Vol of solution(ml)	V (mg/l)	Cr (mg/l)	pH	Vol of solution(ml)	V (mg/l)	Cr (mg/l)	pH	Color
0.24	6.4	25	500	0	110	acidic	500	0	24.4	6-9	slightly yellow
0.29	5.5	25	500	0	110	acidic	500	0	17.0	6-9	slightly yellow
0.45	8.5	25	500	0	110	acidic	500	0	0	6-9	transparent
0.59	7.4	25	500	0	110	acidic	500	0	0	6-9	clear and transparent
0.75	7.6	25	500	0	110	acidic	500	0	0	6-9	clear and transparent
0.24	6.6	25	500	0	140	acidic	500	0	29.28	6-9	slightly yellow
0.29	5.9	25	500	0	140	acidic	500	0	21.4	6-9	slightly yellow
0.45	8.6	25	500	0	140	acidic	500	0	0.94	6-9	transparent
0.59	7.0	25	500	0	140	acidic	500	0	0	6-9	clear and transparent

Table 4 Determined values of settling velocities of V and Cr precipitates

Item / No		Teehni cal				Result
		Temp(℃)	Volume(l)	Flocculant	pH	Settling velocity,mm/min
Ppt of V	1	25	50	no addition	5	6
	2	25	50	addition	5	6.1
	3	25	50	no addition	4	7.3
	4	25	50	addition	4	7.7
Ppt of Cr	5	25	50	no addition	8	16
	6	25	50	addition	8	60
	7	25	50	addition	8	64

Table 5 Analytical data of V precipitate

V precipitate, g	V, %	Cr, %	Fe, %	SiO_2, %	SO_4^{2-}, %	Na^+, %	H_2O, %	Others
81	4.82	0.81	29.69	3.90	14.56	5.97	4.99	35.96
93	4.82	0.89	33.12	3.82	14.77	4.25	7.64	30.69
63	5.59	0.92	35.52	4.32	15.32	5.77	7.73	24.83
63	6.26	0.92	31.69	5.54	12.58	4.98	7.60	30.43
196	3.50	0.53	25.64	3.78	11.85	4.32	6.89	43.49
203	3.30	0.31	24.85	5.82	12.80	5.74	7.56	39.62
121	4.16	1.04	39.36	5.75	11.37	5.05	8.14	25.13
127	4.89	1.21	40.59	4.63	11.97	5.97	7.83	22.91

4.3 Recovery and uilization of precipitates of V and Cr

4.3.1 Recovery and utilization of V

The analytical data of V precipitate is shown in Table 5:

Simulating the heating system of sodium roasting of V slag and leaching condition in actual production, tests on roasting and leaching of the obtained V precipitate were carried out, The reaction is as follows:

$$2Fe(VO_3)_3 + 3Na_2CO_3 = Fe_2O_3 + 6NaVO_3 + 3CO_2\uparrow \quad (6)$$

In small scale test run, the V precipitate is first dried and ground, screened through a 80 mesh sieve, then added with soda and sodium sulfate in the proportion:

V precipitate : Na_2CO_3 : Na_2SO_4 = 50 : 8 : 4

After mixing thoroughly, the materials were placed in an evaporating dish which was loaded in a muffle furnace, kept at a temperature of 300℃ for 1.5 hour. Then the temperature was raised to 800℃ and maintained for 2 hours. Subsequently, the temperature was lowered to 400℃ and kept for 1.5 hour. After roasting, the calcine was leached at 50-60℃ with solid/liquid ratio 1: 2, filtered and washed. Conversion of both roasting and leaching are larger than 95%. The concentration of V in solution is 8-14 g/l with P content of 0.003-0.005 g/l which conforms with the requirement of normal production. For experimental data, see Table 6:

Table 6 Experimental results of leaching

Leaching condition					Experimental results					V Leaching, %
Calcine, g	V, %	S/L	Temp, ℃	Time, min	Residue, g	V, %	Soln, ml	V, g/l	P, g/l	
49.5	5.66	1:2	50-60	15	29.0	0.04	190	8.10	0.0044	99.26
47.3	6.23	1:2	50-60	15	26.5	0.08	180	8.90	0.0032	98.26
40.0	7.12	1:2	50-60	15	20.5	0.182	160	9.21	0.0033	97.67
40.0	9.43	1:2	50-60	15	25.7	0.234	160	14.25	0.0032	96.24
40.0	9.08	1:2	50-60	15	25.6	0.312	160	10.97	0.0049	95.01
40.0	7.87	1:2	50-60	15	25.0	0.65	160	12.38	0.0028	90.81
40.0	6.85	1:2	50-60	15	27.0	0.39	160	1.39	0.0045	93.16
40.0	6.94	1:2	50-60	15	26.5	0.34	160	11.13	0.0047	94.22
40.0	7.12	1:2	50-60	15	25.7	0.31	160	11.20	0.0035	95.02
40.0	7.32	1:2	50-60	15	25.7	0.32	160	12.48	0.0034	96.40

4.3.2 Recovery and utilization of Cr

For analytical data of Cr precipitate, see Table 7:

Table 7 Analytical data of Cr precipitate

Cr precipitate, g	Cr, %	V, %	Fe, %	P, %	SO_4^{2-}, %	Na^+, %	Others
60	31.40	0.56	21.22	0.030	14.25	3.45	29.09
58	31.17	0.34	14.63	0.022	16.03	5.73	32.07
57	30.63	0.04	13.96	0.025	13.35	4.56	37.43
56	30.47	0.24	20.24	0.033	11.80	5.64	31.58

The Cr precipitate mainly consisting of $Cr(OH)_3$ was blended with Cr ore fines, sintered and fed into electric furnace for the smelting of high carbon ferrochromium. No abnormal technical and

economical indexes were found.

5. Industrial application

5.1 Technological flow-process

Based on experimental studies, the process is divided into 2 parts:

5.1.1 Waste water containing V and Cr in the reservoir is pumped to the treatment tank of V. After concentration and filtration, the V precipitate is returned to rotary kiln for roasting.

5.1.2 The upper layer solution containing Cr after treating V is poured into the treatment tank for Cr. After concentration and filtration, the Cr precipitate is blended with Cr orefines to be sintered into lumps and fed into arc furnaces for smelting of ferrochromium.

The flow process is shown in Fig. 2.

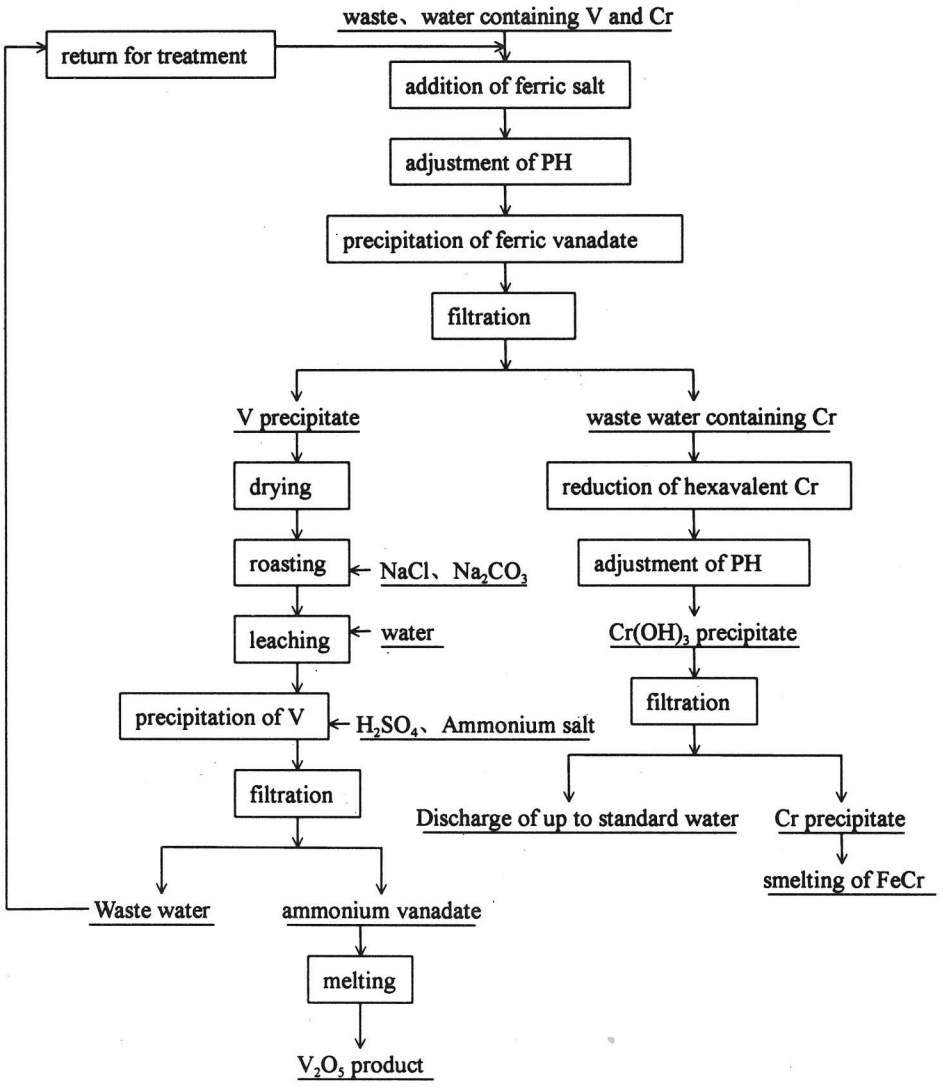

Fig.2 Flowsheet for the treatment of waste water containing V and Cr by 2-step fractional precipitation method

5.2 **Results**

V and Cr in waste water can be completely removed by the 2 step fractional precipitation process. 250-360 tons of waste water are now being treated daily in Emei Co. For the quality of discharged water and the compositions of V and Cr precipitates, see Tables 8 and 9.

Table 8 Quality of discharged water (sampled from the drain in plant) after treatment

V, mg/l	Cr, mg/l	S	NH_3-N	pH	Oil	Smell	Color
0	0	290—310	930—1400	6—9	none	normal	clear and transparent

Table 9 Composition of V and Cr precipitates

	Wet sample, g	H_2O, %	Dry sample, g	V, % in dry sample	Cr, % in dry sample
V PPt	100	81.6	18.4	9.14	3.45
Cr PPt	100	82.4	17.6	0.94	17.6

5.3 **Utilization of V and Cr precipitates**

5.3.1 **Utilization of V**

V precipitate after filtration is mixed with V containing dust from electrostatic precipitator and then fed into rotary kiln for roasting. The production process and product quality have always been regular. The comprehensive recovery of V is over 87%.

5.3.2 **Utilization of Cr**

Since Cr precipitate has a high water content, it would cause splashing if directly fed into the furnace for smelting and would become fine particles after high temperature drying, influencing the permeability of furnace charge and escaping mostly with furnace gas to cause loss and difficult recovery. Consequently, since 1992 the Cr precipitate is mixed in suitable proportion with Cr ore fines from South Africa (containing Cr_2O_3 42.85%) and sintered to lumps, blended with other Cr ores and fed into arc furnace for smelting to ferrochromium. Both production process and product quality are regular. The comprehensive recovery of Cr is over 85%.

6. Some problems deserving attention

6.1 **Determination of the pH at which Cr precipitates**

From handbook, it was found that the solubility product of $Cr(OH)_3$, $pKs \doteq 30.2$ At pH = 6, -log $[Cr^{3+}] = 6.3$, $[Cr^{3+}] = 6.3 \times 10^{-7}$ mol = 32.7 mg/l

At pH = 6.5, $[Cr^{3+}] = 1.03$ mg/l

At pH = 7, $[Cr^{3+}] = 0.033$ mg/l

Comprehensive tests on the Cr content and suspension content of the upper layer of solution containing Cr precipitate were made. The results are shown in Table 10.

Table 10 Contents of Cr^{3+} and suspension of discharged water at different pH

pH	5.5	6	6.5	7	8	9
Cr(mg/l)	micro	micro	micro	0	0	0
Suspension(mg/l)	micro	micro	105	185	425	546

The data from handbook and experimental work have shown that at pH 7, Cr^{3+} content of the upper layer solution completely conforms with the requirement of discharge standard and the water is clear and transparent with few suspensions; At pH > 7, the upper layer solution will become turbid, with a great deal of fine particles of hydroxide colloids floating. According to the experience of Jinzhou Ferroalloy Co., it is found that $Cr(OH)_3$ precipitate begins to form at pH = 5.3. From data in table 10, it can be seen that when pH is too high, the content of suspension will greatly exceed the standard and the consumption of alkali will also greatly increase. Especially for the waste water

containing high concentration of Cr, the condition will become much more serious. It has also been shown from operating practice that best result will be achieved when the pH at which Cr precipitates is controlled at 7.

6.2 **Control of suspension in dischsrged solution**

The suspension comes from those brought out by directly discharged upper layer solution from the tank of precipitating Cr and those brought out by the filtrate after filtering the sludge of Cr precipitates. Since Cr precipitate is of loose structure, it is still a fluffy mass accumulated at the bottom of tank after settling from water. When discharging the upper layer solution, the hydraulic pressure at the bottom is relatively large, resulting in part of Cr precipitate brought out from the discharging of the upper layer solution. Therefore, multi-holes should be considered in the designing of precipitating tank to discharge successively from the upper layer to the lower layer. The discharged suspension is markedly lowered after increasing the number of holes from 1 to 3. See Table 11.

6.3 **Corrosion protection of transport equipment**

Owing to the characteristics of the process, the corrosion of equipment is very serious; especially the pump for transferring corrosive liquid is quickly corroded and damaged, the average life being only around 3 months. Change of reagent and use of bakelite pump have been tried in vain. At present the use of pneumatic transport and bakelite pipes is quite effective.

Table 11 Comparison of suspension content in discharged solution with different no. of holes

Suspension content in discharged solution from 1 hole, mg/l	Suspension content in discharged solution from 3 holes, mg/l
460	305
1278	273
2780	294
930	132
2063	268

Conclusions

1. Technological process of treatment of waste water containing V and Cr by 2 step fractional precipitation is feasible with quality of discharged water conforming to standard and meeting the requirement of industrial production. 100,000 tons of waste water can be treated annually with the existing equipment in Emei Co.
2. Control of the end point of pH of solution at 7 when precipitating Cr will effectively control the suspension content in solution.
3. V and Cr precipitate can be recovered and utilized without secondary pollution. The process also has certain economical benefit.

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