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Treatment of manganese wastewater from titanium dioxide plant using complex phosphate

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Abstract: The acidic wastewater containing manganese and other heavy metal ions came from the plant which produce titanium dioxide in the method of the sulfuric acid digestion was disposed under the processes of the pre-neutralization with the mineral containing phosphorus and calcium, alkaline precipitation and re-regulating pH with the raw wastewater. The removal ratio of manganese and ferrous were higher than 99% and 98%, respectively, when the concentration of manganese and ferrous were 46 mg/L and 2000 mg/L. More than 5800 mg/L of SO_4^{2-} were neutralized also. The effluent pH was the range between 6 and 9, the concentration of other pollution substances were all very lower even have not discoveried.

Key words: phosphorite; titanium dioxide; manganese; wastewater

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Introduction

Using complex phosphate to treat manganese wastewater from titanium dioxide plant was presented in this paper. Comparing with other normal treatment methods, this technology get to such aid that the pH neutralization and sedimentation of some mangnese can be finished and the sediments can be separated from the liquid easily. The wastewater was used at the process of pH pre-adjusted and the contents of remained pollutants was low to meet the national standard. It should not ignore that the mineral which obtain easily and price cheap substitute for the pure compound completely to reduce the alkali consume in the alkaline precipitation stage.

1 The sources and the quantity of wastewater

The limenite and sulfuric acid are the main raw material for production titanium dioxide by means of the method of sulfuric acid digestion. Some manganese and other heavy metal ions of ore were turned to the waste sulfuric acid and others into the sewage in the hydrolysis workshop section after digestion by sulfuric acid. The characteristic of wastewater was higher acidity, the higher chromaticity and contained a kinds of metal ions. Table 1 shows the practical data determined by methods of atomic absorption spectrometry and chemical analysis, the samples came from a plant were the two-days-in-one complex sewage continuously.

It can be seen from Table 1 that the concentration of SO_4^{2-} in the wastewater exceeded the national standard seriously. It converted into sulfuric acid(98%, more than 6040 mg/L). The manganese and chromium were 8 times and 4 times of national standard respectively. The other heavy metal ions were all lower than the range of national standard for wastewater discharge except such the metal ions as iron, titanium, vanadium and so on.

2 Reaction principle for removal pollutant

2.1 Pre-neutralization sulfuric acid with alkaline materials

In order to remove manganese, the waste acid decomposed from the sulfate must be neutralized to increase the pH value.

$$H_2SO_4 + CaCO_3 \rightarrow CaSO_4 \downarrow + CO_2 \uparrow + H_2O. \quad (1)$$

The carbonate of lime can be precipitated by itself and formed many kinds of heavy metal ions. Table 2 shows that $[(CO_3)^{2-}]$ released from carbonate of lime can react with the ion of manganese and iron to produce weak carbonate salt which solubility is 100 to 1000 times less than the carbonate of lime itself.

Table 1 Sewage quality

Item	Concentration, mg/L	Standard(GB8978-88, China)
pH	1.6—1.8	6—9
SO_4^{2-}	5800	1.0
Fe	2000	–
Ti	128	–
Mn	46	5.0
Cr	2.2	0.5
V	3.1	–
Cu	0.7	0.5
Cd	0.1	0.1
Zn	1.35	2.0
Pb	0.5	1.0
Hg	0.004	0.05
Sn	ND*	2.0
Sb	ND	–

*: not be discoveried

Table 2 The solubility product of some carbonate

Carbonates	K_{sp}
$CaCO_3$	2.8×10^{-9}
$MgCO_3$	3.5×10^{-8}
$FeCO_3$	3.2×10^{-11}
$MnCO_3$	1.8×10^{-11}

2.2 Exchange precipitation

Based on the law of solubility product, the compound with small solubility product will deposite firstly under the condition of the same concentration of metal ion and precipitant, then exchange precipitation took place. When the existence of metal salt with greater solubility product and the metal ion which can be produce another salt with smaller solubility, the salt with greater solubility will dissolve and free the anion. The negative ion and another metal ion produce a chemical compound with even more petty solubility product.

Based on Table 2, under pH 7.15, the reaction is as follows:

$$Ca_3(PO_4)_2 \rightleftharpoons 3Ca^{2+} + 2(PO_4)^{3-}, \quad (2)$$

$$(PO_4)^{3-} + Mn^{2+} \longrightarrow Mn_3(PO_4)_2 \downarrow, \quad (3)$$

$$Ca_3(PO_4)_2 + MnSO_4 \rightleftharpoons CaSO_4 + Mn_3(PO_4)_2 \downarrow. \quad (4)$$

2.3 Alkaline take off the manganese

It can bee seen from Fig. 1 when the pH value was between 10 to 11, the $[Mn^{2+}]$ in solution was 10^{-6} to 10^{-7} mol/L. The Zn, Ni and Fe etc. will be sedimented preceeding manganese in the process of pH value going up.

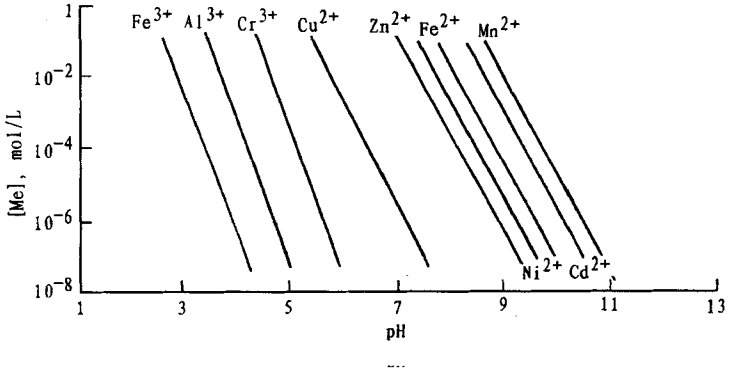

Fig. 1 The relationship between metal solubility and pH value

3 Test conditions

Using the phosphorite, limestone and dolomite for treatment manganese precipitant instead of pure chemical compound. Two kinds of mineral be used after smashed. The results determined with flame atomatic absorption spectrometry are shown in Table 3.

The normal equipments, vessels and other motor machine such as the magnetic stirrer in laboratory be used for the test.

Table 3 Mineral parameters

Contents, %	Phosphorite	Limestone
ND*	17.36	
CO_2	3.48	
P_2O_3	29.35	
CaO	42.63	53.10
MgO	0.63	2.06
Al_2O_3	0.83	0.18
Fe_2O_3	0.44	0.63

* : not be disoluted by acid

4 Results

4.1 Pre-neutralization results

4.1.1 The limited removed result in single mineral

Adding over amount of dolomite, phosphorite and limestone into three vesseles with the same kinds of wastewater respectively. The pre-neutralization results are shown in Table 4.

The pH values were 3.0, 4.8 and 5.8 varied as the order of the dolomite, phosphorite and limestone respectively. The ferrous remains concentration from low to high as the order of phosphorite, limestone and dolomite and the removed ratios are 98.1%, 88.9% and 64.9% respectively. The remains manganese concentration are all on the same level, among of all the remains concentration the result added the dolomite is the lowest, 11.2 mg/L. The remains concentration of added phosphorite and limestone added are 13.13 mg/L and 13.16 mg/L, both of them no any difference. The manganese removed ratios are 85.7%, 71.5% and 71.4% as the order of added dolomite, phosphorite and limestone respectively.

4.1.2 The limited removed result for mix pre-neutralization

Table 5 shows the result of adding 20 g limestone and 10g phosphorite in one liter wastewater.

Compare with Table 4, the pH value of the supernatant of the test sample of mixed pre-neutralization is the same as added phosphorite only, the remains concentration of manganese ion is the same level as the added phosphorite and limestone alone, total ferrous removed ratio is 98.5%, not only little higer than the result of adding phosphorite, but also higer than adding limestone (33.6%) and dolomite (9.6%), respectively.

Table 4 Pre-neutralization results of single mineral

Item	pH	Fe^{2+}, mg/L	Mn^{2+}, mg/L
Raw wastewater	1.67	1749.5	46
Dolomite	3.0	194	11.2
Phosphorite	4.8	32.4	13.13
Limestone	5.8	614.7	13.16

Table 5 The results of mixed pre-neutralization

Item	pH	Fe^{2+}, mg/L	Mn^{2+}, mg/L
Raw wastewater	1.67	1749.5	46
Supernatant	4.7	25.9 (Tot.)	13.09
Removed ratio, %		98.5	71.5

4.2 The relation of remains manganese and pH value

Take the four parts of pre-neutralization samples, adjust their pH value to 8, 9, 10 and 11 in sodium hydroxide respectively. The remains manganese concentrations under the various pH values are presented in Fig.2.

The remains of manganese is less than 1 mg/L, even have not discoveried when the pH value

more than 10.

4.3 The relationship of adding sodium hydroxide and re-adjusting the pH of pre-neutralization sample

Fig. 3 introduces the relationship of the pH value and adding sodium hydroxide in the sample of pre-neutralized.

The pH value of wastewater was higher than 10 when the sodium added was about 1200 mg/L.

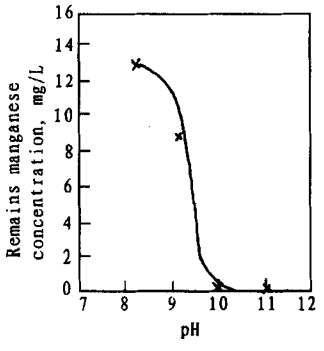

Fig. 2 Relationship between pH values and remained manganese content

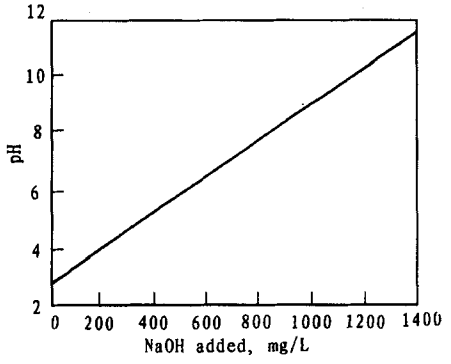

Fig. 3 The relationship of pH value and adding sodium hydroxide

4.4 Re-adjustion pH with the raw wastewater

The wastewater pH 10 was higher than the national standard for drain wastewater in the period of alkaline disposed manganese. Therefore, it must be re-regulation to the range of pH 6 to 9 before discharge. Table 6 lists the two groups test data titrated with the raw wastewater in the supernatant after the alkaline remove manganese.

Table 6 The results of re-adjustion pH

Content	No. 1	No. 2
Sample pH*	9.37	9.0
Ratio of add raw wastewater, %	0.15	0.44
pH after added raw wastewater	9.0	5.4
$[Mn^{2+}]$(mg/L) after added raw wastewater	ND	0.2112

*: sample was the alkaline remove manganese wastewater at the time the pH was 10.7 but it reduced to the value in Table 6 after 20 h

The sample pH value should be re-regulation to 9.0 to 5.4 in the range of 0.15% to 0.44% of the ratios of raw wastewater to the sample. The releave manganese content: test No. 2 is only 0.2112 mg/L, when pH be re-regulated to 5.4; based on the test data and Fig. 2, the contents of No. 1 were lower than test No. 2.

In a word, the pH and manganese ion are lower than the national standard for waste discharge, when the ratio of the raw wastewater re-regulated be controlled at 0.30%.

4.5 Sediments character

In order to simulate the processing course, threw the sodium hydroxide into the three liters of pre-neutralization sample which did cleaned of the sediments get the pH more than 10, pour it into a test tube to observe the precipitant character, then determined sediments character. The results showed that the alum-flower of sediments is more greater and the demarcation face between the clear liquid and muddy liquid was obvious. After the sedimentation time of 40 minutes, 2h and 20 h, the volume ratio of sediments were 50%, 27% and 18.3%, respectively.

The sediments data after 20h are shown in Table 7.

Table 7 The character of sediments

Item	Data
Volume, ml	549
Volume ratio, %	18.3
Dry weight, g	32.5
Moisture, %	94.5
Sediment produce ratio, mg/L	10830

4.6 Materials consumption

The materials consumption of every test stage is listed in Table 8.

Table 8 Quatas of materials consumption

Stage	Pre-neutralization		Re-regulating pH
Material	Limestone	Phoshorite	Sodium hydroxide
Consumption, g/L	20	10	1.2

5 Conclusion

The acidic wastewater containing manganese and other heavy metal ion came from titanium dioxide plant in sulfuric acid digestion was disposed under the processes of the pre-neutralization with phosphorite and limestone, alkaline precipitation and re-regulating pH with the raw wastewater. The removal ratios of manganese and ferrous were higher than 99% and 98% when the concentration of manganese and ferrous were 46 mg/L and 2000 mg/L respectively. More than 5800 mg/L waste sulfuric acid were neutralized also. The effluent pH was the range between 6 and 9, the concentration of other polluted substances were all very lower even have not discoveried.

In the stage of mixed pre-neutralization when the add amount both of the limestone and phosphorite were 2% and 1% respectively, the wastewater pH value can get to 4.7, the removed ratio of ferrous and manganese can get to 71.5% and 98.5%, respectively.

In the stage of alkaline disposed manganese adding sodium hydroxide 1200 mg/L into the pre-neutralized wastewater, its pH can be higher than 10, the manganese content in the supernatant will be trace amount.

Adding 0.3% of raw wastewater to re-regulate the alkaline disposed manganese waste samples can steady the pH value of discharge out in the range of 6 to 9. The concentration of manganese ion and other heavy metal ions were all lower than the national standard for wastewater discharge.

The formed ratio of the sediments of the wastewater was 10830 mg/L.

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