



PRETREATMENT OF WASTEWATER FROM HEAVY-OIL-PYROLYSIS-GAS-MAKING SYSTEM

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ABSTRACT

It was found that the process of pressure-hydrolysis failed for the treatment of a wastewater containing cyanide and nickel from heavy-oil-pyrolysis-gas-making system. The analysis of the wastewater showed the existence of Ni^{2+} , CN^- , NH_3 , Ca^{2+} and HCO_3^- . Therefore, the coordinate compounds of $[\text{Ni}(\text{CN})_4]^{2-}$ and $[\text{Ni}(\text{NH}_3)_n]^{2+}$ could be expected. Considering the Ca^{2+} and potential CO_3^{2-} transformed from HCO_3^- , it was not surprising that white precipitate blocked the pipeline within the pressure-hydrolysis process under the condition of high pH. A pretreatment step of calcium removal was suggested. Various factors were investigated and optimal operational conditions were concluded. After calcium was removed, the treatment processes were operated successfully and satisfactory results obtained. The residual concentrations of Ni^{2+} and CN^- could be reduced to meet the discharging standards. © 1997 IAWQ. Published by Elsevier Science Ltd

KEYWORDS

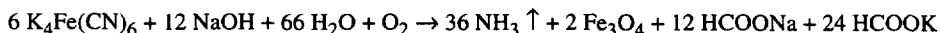
Calcium precipitation; cyanide; nickel; pressure-hydrolysis; pretreatment; wastewater.

INTRODUCTION

In petrochemical plants, fertilizer (ammonium bicarbonate) could be produced by CO_2 and NH_3 obtained by heavy oil via pyrolysis. In the gas-making process, a certain amount of wastewater containing cyanide and nickel salts will be formed. This kind of wastewater should be treated carefully and then discharged properly into the natural water body or municipal system since both cyanide and nickel salts are very toxic and harmful to human beings and aquatic animals.

The wastewater with high concentration of cyanide is usually treated by recovery process via $\text{Na}_4[\text{Fe}(\text{CN})_6]$ or $\text{K}_4[\text{Fe}(\text{CN})_6]$ (Yu, 1979), in which the removal efficiency of cyanide can reach 80-90% and 20-30 mg/l of residual cyanide still exists in the effluent. The acidification-distillation process could also be used and hydrogen cyanide is recovered (Zhu, 1992). The wastewater with lower concentration of cyanide can be treated by the processes of alkaline chlorination (Tu, 1989), ozonation (Gurol *et al.*, 1985), electrolysis-oxidation (Yu, 1979), pressure-hydrolysis and biological treatment (CNEPA, 1991), ion exchange (Fan, 1984), activated carbon catalysis-oxidation (Zhou, 1980), etc. For the treatment of nickel containing wastewater, chemical precipitation (Ning, 1985), ferrite process (Cao, 1983), etc. could be adopted. But chemical precipitation is mostly used because of its simple operation, lower cost and precipitate recovery.

According to the report (Zhu, 1992), the pressure-hydrolysis was effective for cyanide removal, which was operated under the conditions of pH >9.5, T=140-180°C and P=0.4-1.0 MPa. The original wastewater contained 71-110 mg/l of CN⁻. After the treatment, the effluent was obtained with CN⁻ less than 0.5 mg/l. It was important to control the pH of wastewater. If adequate alkali existed, not only the cyanide containing coordinate compounds could be destroyed, but also volatile CN⁻ would be hydrolyzed. The reaction equations are shown as following:



In a petrochemical plant, the processes of pressure-hydrolysis and neutralization-precipitation were used to treat the wastewater containing cyanide and nickel. However, it was found that such kind of processes were not as effective as expected and white precipitate blocked the pipeline at the stage of pressure-hydrolysis. The quality of effluent could not meet the discharging standards. It seems necessary to pre-treat the wastewater before the pressure-hydrolysis process.

EXPERIMENTAL

Wastewater

WWA, wastewater from the gas-making process, 25 m³/h; WWB, wastewater from the transformation of CO to CO₂, 15 m³/h; WWC, effluent from high-pressure reactor after the pressure-hydrolysis of WWA.

Apparatus

High-pressure reactor (1 l, with electromechanical stirrer, external oil-bath heating, automatic temperature control), pH meter, electromagnetic stirrer with heating, steam-distillation column (Ø=20 mm, H=1000 mm, h(pack)=800 mm).

Analytical methods

Ca²⁺ and Ni²⁺ was measured by atomic absorption spectrophotometer. The sample was distilled at pH=4 with the existence of Zn(NO₃)₂, absorbed by NaOH solution and then volatile CN was determined by titration with AgNO₃. The sample was distilled at pH < 2 with the co-existence of H₃PO₄ and EDTA, absorbed by NaOH solution and then total cyanide was decided by titration with AgNO₃. NH₃-N was measured by ammonia-sensitive electrode. TKN was determined by Kjeldahl method. CO₃²⁻ and HCO₃⁻ were decided by acid-alkali titration with different indicators. COD was determined by potassium dichromate method.

Test

Calcium removal. Alkali (30% NaOH solution) was added into WWA or the mixture of WWA and WWB (4:1) in beakers with stirring and heating, respectively. White precipitate of Ca(OH)₂ was removed by filtration.

Pressure-hydrolysis of cyanide. After calcium removal, the wastewater was transformed into the high-pressure reactor and hydrolyzed at the conditions of P=1.0 MPa(gauge), T=180°C and stirring velocity of 420 n/min. The pressure-hydrolysis was carried out as the scheme shown in Figure 1.

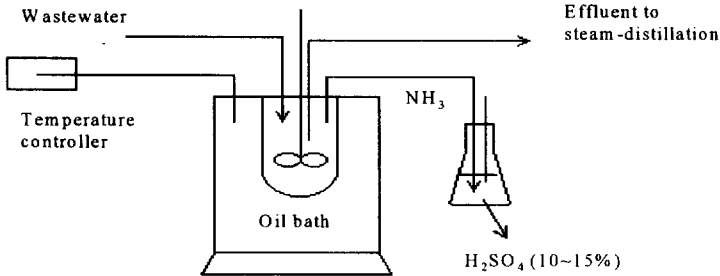


Figure 1. The scheme of pressure-hydrolysis.

Steam-distillation of ammonia. After cyanide was removed, the wastewater was steam-distilled with waste steam of 0.12-0.16 Map (gauge) and its scheme is illustrated in Figure 2. The test column was packed with ceramic rings of 5 x 5 x 1 mm in size.

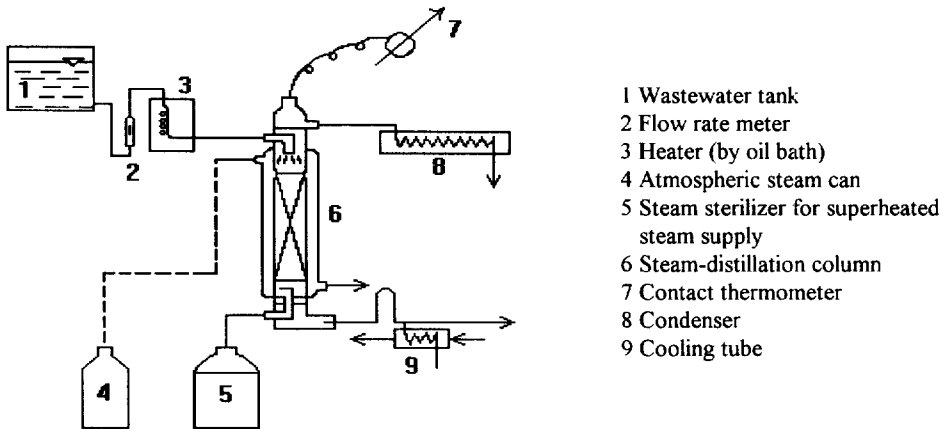


Figure 2. The scheme of steam-distillation.

RESULTS AND DISCUSSION

Analysis of wastewater

The samples of WWA and WWB were provided in four different batches by the petrochemical plant and that of WWC once. The analysis results of wastewater composition are shown in Table 1, from which it can be seen that the WWA was near neutral condition (pH=7.48-8.41). Besides the existence of Ca^{2+} , Ni^{2+} , CN^- and NH_3 , there was a certain amount of HCO_3^- . The pH of WWB was in the range of 8.35-9.43 and the major components were CO_3^{2-} , HCO_3^- and NH_3 . Investigating the analysis results of WWA, there were differences between CN^-_{v} (volatile) and CN^-_{T} (total), and between $\text{NH}_3\text{-N}$ and TKN, which implied that part of CN^- and NH_3 appeared in the form of coordinate compounds as $[\text{Ni}(\text{CN})_4]^{2-}$ and $[\text{Ni}(\text{NH}_3)_n]^{2+}$. The formation constant of $[\text{Ni}(\text{CN})_4]^{2-}$ is 31.3 and those for $[\text{Ni}(\text{NH}_3)_n]^{2+}$ are 2.80 to 8.74 corresponding to $n=1-6$, respectively (Dean, 1985). If the pH of WWA is increased high enough, the coordinate compounds could be destroyed and volatile CN^- would be hydrolyzed in the process of pressure-hydrolysis. And then NH_3 can be removed by steam-distillation.

Table 1. Analysis results of wastewater

Samples of wastewater	pH	Ca ²⁺ mg/L	Ni ²⁺ mg/L	CN _v mg/L	CN _T mg/L	CO ₃ ²⁻ mmol/L	HCO ₃ ⁻ mmol/L	COD mg/L	NH ₃ -N mg/L	TKN mg/L
WWA1	8.41	33.0	21.9	8.28	13.15	ND	33.55	910.4	537.0	691.0
WWA2	7.64	42.0	14.3	16.07	18.04	ND	22.94	905.7	416.9	630.2
WWA3	7.65	59.3	25.2	11.98	12.72	ND	10.19	1140	562.3	852.1
WWA4	7.48	24.8	17.3	17.14	24.05	ND	10.39	873.5	977.0	1053
WWB1	9.34	ND	0.7	3.97	5.75	484.1	176.4	692.3	1.17*10 ⁴	1.58*10 ⁴
WWB2	9.43	0.9	0.2	1.51	2.02	303.2	60.48	592.3	1.04*10 ⁴	1.12*10 ⁴
WWB3	8.68	0.64	ND	3.47	10.62	542.7	232.8	873.7	2.09*10 ⁴	2.14*10 ⁴
WWB4	8.35	0.5	ND	3.85	7.54	435.2	121.8	790.3	1.99*10 ⁴	2.23*10 ⁴
WWC1	8.27	32.4	14.4	11.49	12.38	ND	26.99	780.4	478.6	660.7

Consideration of the failure of pressure-hydrolysis

Comparing the analysis results of WWA1 with that of WWC1, it can be noticed that the pHs of these two streams are very close (8.41 and 8.27), and the Ni²⁺ and CN were almost not removed. It seems that the plant kept the pressure-hydrolysis at relatively low pH in order to avoid the blocking of the pipeline, nevertheless, this could not meet the requirement of pressure-hydrolysis. Therefore, more alkali should be added to increase the pH of WWA. Due to the existence of Ca²⁺ and HCO₃⁻, the precipitates of Ca(OH)₂ and CaCO₃ may be considered, which solubility products are 5.5×10⁶ and 2.9×10⁹ (Dean, 1985), respectively. It can be told by calculation that the precipitate of Ca(OH)₂ could not appear at the pH of WWA with such concentration of calcium. If calcium must be removed, the pH should be higher than 12.9. According to stoichiometry, 0.825 mmol of CO₃²⁻ is needed to form the precipitate of CaCO₃ in WWA1. Higher concentration of CO₃²⁻ would be required to reduce the concentration of calcium ion to the designated lower limit. It can also be noticed that the concentration of CO₃²⁻ was not detected in WWA, but a certain amount of HCO₃⁻ existed. Thus there is a potential of obtaining CO₃²⁻ via the transformation of HCO₃⁻ by adding alkali. This is the reason why the pipeline was blocked by white precipitate during the operation of pressure-hydrolysis. In order to assure a successful treatment, it is necessary to pre-treat the WWA by calcium removal.

Calcium removal

Determination of optimal dose of alkali. Since the pair of CO₃²⁻ and HCO₃⁻ could form a buffer solution, a certain amount of alkali was required to release CO₃²⁻. And then the pH of WWA increased. Figure 3 shows a typical curve of pH of WWA (200 ml) vs. added volume of 30% NaOH solution.

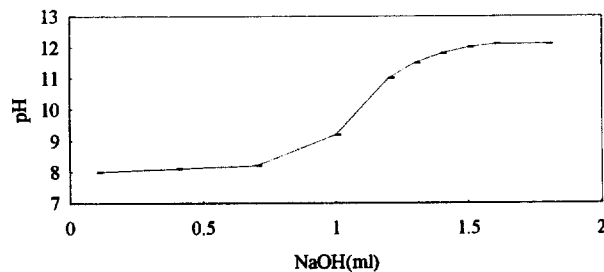


Figure 3. pH of WWA vs. added volume of 30% NaOH solution.

Investigating this curve, a rapid jump can be found near pH=9.5. And the smell of ammonia could be detected during the experiment. This may indicate that in this complicated system ammonia was mainly

released and the destruction of the coordinate compounds occurred. Then, at pH=10.80, the wastewater became turbid obviously due to the precipitate of CaCO_3 , which implies that CO_3^{2-} was transformed from HCO_3^- . At this point, 1.8 kg NaOH/m^3 WWA was consumed, but bad settling of the precipitate was observed. Since this curve was obtained at room temperature, the flock of CaCO_3 grew up slowly. Considering more alkali consumed by the succeeding processes of pressure-hydrolysis and steam-distillation, it is better to adjust the wastewater to pH=12 at the stage of calcium removal, and the consumption of alkali would be 2.7 kg NaOH/m^3 WWA.

Temperature influence. To investigate the temperature influence on calcium removal, a series of experiments at different temperatures were carried out. The results is shown in Table 2.

Table 2. Temperature influence on calcium removal

NO.	WWA mL	WWB mL	T °C	Alkali added mL	pH	Settl. time min.	Ca ²⁺ mg/L	Ni ²⁺ mg/L	NH ₃ -N mg/L	CO ₃ ²⁻ mmol/L	HCO ₃ ⁻ mmol/L	COD mg/L
A	200	/	20	2.00	12.26	30	3.2	7.2	195.7	18.8	ND	820.7
B	200	/	50	1.83	12.05	30	1.4	6.5	141.4	16.8	ND	880.2
C	200	/	70	1.82	12.02	30	0.3	7.3	74.3	16.6	ND	857.5
D	200	/	80	1.90	12.09	15	0.2	7.3	70.7	13.8	ND	844.4
E	200	/	90	1.80	12.01	15	0.2	6.0	68.3	13.4	ND	832.5
1	200	/	70	1.82	12.21	30	1.1	8.0	398.1	8.48	ND	1100
2	200	/	80	1.77	11.97	15	1.2	8.0	100.0	6.98	ND	1196
3	200	/	90	1.82	12.01	15	1.3	8.4	162.2	8.32	ND	1131
4	1000	/	90	9.00	12.11	20	1.1	7.4	N/A	7.12	ND	1243
5	200	50	70	10.58	11.95	30	0.7	12.3	955.0	139.2	ND	942.5
6	200	50	80	10.40	11.96	10	0.7	9.6	524.8	156.8	ND	990.0
7	200	50	90	10.55	11.90	10	0.5	12.4	645.7	128.6	ND	1133
8	1000	250	90	52.60	12.00	20	0.5	8.2	N/A	137.5	ND	974.2

Note: WWA2 and WWA3 were used in Exp. A-E and Exp. 1-8 respectively.

It can be seen that the removal efficiency of calcium ion increases slightly with temperature increase. At higher temperatures (70-90°C), the residual concentrations of calcium ion are reduced to the level of 1 mg/l and did not vary much with temperature. Furthermore, the settling property of CaCO_3 precipitate was improved, especially at 90°C. Since the formed flocks moved fast and the opportunity of contact-collide with others increased, the flocks would grow up quickly in size. On the other hand, the temperature of original WWA is close to 90°C, which could be utilized for calcium removal. In addition, it could be noticed that the concentration of nickel ion was also reduced significantly during calcium removal.

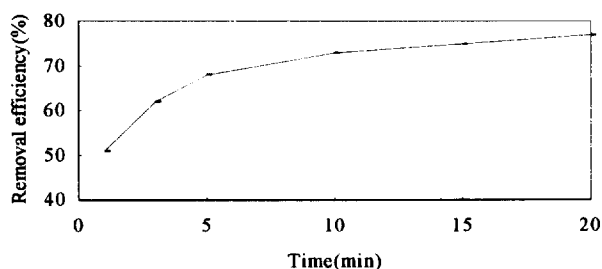


Figure 4. Calcium removal efficiency vs. settling time.

Settling time. When calcium removal was operated at higher temperatures, thermal movement of the flocks occurred during the process. Figure 4 shows the curve of calcium removal efficiency vs. settling time. It indicates that the removal efficiency of calcium was greater than 75% when the settling time reached 15-20

minutes. To extend the settling time any longer, the removal efficiency could not be improved much. The thermal movement may make small flocks unsettling.

Calcium removal at high concentration of Calcium ion. According to the information provided by the plant, the composition of WWA fluctuated frequently in a wide range. In the extreme case, the concentration of Ca^{2+} could reach 250 mg/l. In order to assure the removal of Ca^{2+} , it was necessary to investigate this case. The experimental data are shown in Table 3. These wastewater samples were obtained by adding adequate calcium ion into WWA3.

Table 3. Calcium removal of the wastewater with 253.3 mg/l of calcium ion

NO.	WWA mL	WWB mL	T °C	Alkalia added mL	pH	Settl. time min.	Ca^{2+} mg/L	Ni^{2+} mg/L	$\text{NH}_3\text{-N}$ mg/L	CO_3^{2-} mmol/L	HCO_3^- mmol/L	COD mg/L
1	200	/	90	2.12	11.99	15	0.7	7.2	151.4	6.41	ND	1314
2	200	50	90	10.05	12.00	12	0.3	6.0	1047	108.3	ND	1236
3	200	50	80	10.65	12.01	12	0.3	7.0	1513	127.4	ND	1168
4	200	50	70	10.80	12.00	30	0.3	9.1	1122	127.4	ND	1156

The results indicate that even when the concentration of Ca^{2+} was higher than 250 mg/l, the removal of calcium was still effective. For example, the concentration of HCO_3^- was 10.19 mmol/l in WWA3 (CO_3^{2-} was not detected, shown in Table 1). If the HCO_3^- could be totally transformed into CO_3^{2-} , it was more than the requirement of precipitating calcium since the concentration of Ca^{2+} was only 6.33 mmol/l. If a lower concentration of Ca^{2+} is preferred, e.g. 0.1 mg/l, a higher concentration of HCO_3^- will be required. This extreme case with high concentration of calcium ion, of course, does not always happen. Hence, the concentration of CO_3^{2-} can usually meet the requirement. In case there is a shortage of CO_3^{2-} in WWA, WWB with abundant CO_3^{2-} and HCO_3^- needs to be introduced to make a remedy. However, the amount of alkali added will increase significantly. In the experiments, the volume ratio (WWA/WWB) of four was adopted and the consumption of alkali was about five times of that required by WWA only. The discussion above implies that the concentration of HCO_3^- is an important parameter to control the process of calcium removal.

From the discussion of experimental results, the optimal operation conditions for calcium removal can be concluded as following: pH=12 may be adjusted for WWA with the consideration of alkali consumption in the succeeding processes; the temperature of the wastewater needs to be kept at 90°C and the settling time of 30 minutes is suggested. If the concentration of HCO_3^- is not high enough in WWA and lower concentration of Ca^{2+} in effluent is required, WWB may be introduced to assure the calcium removal. In this case, the cost of alkali consumption should be considered. Significant reduction of nickel ion during calcium removal would be favorable to the succeeding treatments.

Pressure-hydrolysis test for cyanide

After calcium removal, the pretreated wastewater was hydrolyzed in the high-pressure reactor, at $T=180^\circ\text{C}$ and $P=1.0\text{ MPa}$ with the residence time of 40 minutes. The results showed that after pressure-hydrolysis, the concentration of volatile CN^- was reduced to meet the discharging standard ($<0.5\text{ mg/l}$) in either case of WWA only or the mixture of WWA and WWB (4 : 1). Attractively, the calcium ion was not detected and the concentration of Ni^{2+} was reduced to the level for discharging, which means that further treatment of nickel ion is unnecessary. Besides, a small amount of dark precipitate was found at the bottom of the reactor, which may include CaCO_3 , $\text{Ni}(\text{OH})_2$ and impure metal hydroxides.

Test in series

In order to check the feasibility of the whole treatment process, a test in series (calcium removal - pressure-hydrolysis - steam-distillation) was carried out. The results are listed in Table 4.

Table 4. The results of test in series (WWA4)

Treatment	WW volume mL	Alkali added mL	v / w	pH	Ca ²⁺	Ni ²⁺	NH ₃ -N	CO ₃ ²⁻	HCO ₃ ⁻	CN _v ⁻	CN _T
Calcium removal	18750	166.8	/	12.08	0.53	7.3	524.8	9.06	ND	N/A	N/A
Pressure hydrolysis	18000	/	/	11.67	ND	0.15	N/A	N/A	N/A	0.3	0.98
Steam distillation	18000	/	1:4	11.45	ND	0.15	50.1	N/A	N/A	N/A	N/A

Note: v/w is the volume ratio of condensate to wastewater instead of that of steam to wastewater.

The steam-distillation was conducted in the steam-distillation column with the wastewater flow rate of 4 l/h, pH >11 and the feed temperature of 95°C at the top of the column. After the series of treatments, the concentration of NH₃-N could be reduced to meet the discharging requirement designated by the plant. The major pollutants of nickel and cyanide were almost removed and their residuals would be satisfied by the discharging standards. It means that the pretreatment of calcium removal makes the whole treatment process successful.

CONCLUSION

Based on the wastewater analysis and theoretical consideration, the failure of pressure-hydrolysis process for cyanide was found to be due to the pipeline blocked by the precipitate of CaCO₃. Hence, the pretreatment of calcium removal was suggested. The optimal operational conditions were suggested. Calcium removal may be operated at pH=12, which would be concordant with the succeeding processes. The temperature is chosen as 80-90°C and 30 minutes of settling time of precipitate would be required. In a general case, the concentration of HCO₃⁻ in WWA can usually meet the requirement of calcium precipitation. Otherwise, a certain volume ratio of WWB may be introduced to be mixed with WWA and high concentrations of CO₃²⁻ and HCO₃⁻ in WWB could be utilized. However, more alkali will be consumed and the cost should be taken into account.

Based on the experimental investigation, the whole treatment process is suggested as: calcium removal by precipitation - pressure-hydrolysis for cyanide - steam-distillation for ammonia. Through the series of treatments, the major pollutants of nickel and cyanide can be removed and their residuals will meet the requirements of discharging standards. Further treatment of precipitation for nickel, as the plant did, is unnecessary.

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