academicJournals

Vol. 9(12), pp. 581-585, 30 June, 2014
DOI: 10.5897/SRE2014.5981
Article Number: 2FE5F9045699
ISSN 1992-2248 © 2014

http://www.academicjournals.org/SRE

Scientific Research and Essays

Full Length Research Paper

Recycling sodium dichromate in sodium chlorate crystallization mother liquor by nanofiltration membrane

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Received 19 May, 2014; Accepted 11 June, 2014

In the process of sodium chlorate electrolysis production, chemical precipitation is often used to remove the sulfate radical in the crystallization mother liquor which leads to the dichromate deposit to salt sludge together with sulfate, and finally causes chromium pollution. The nanofiltration membrane and freezing crystallization integrated technology was presented to treat crystallization mother liquor. The research conducted in this work shows that, $Na_2Cr_2O_7$ concentration was lower than 0.05 g/L, Na_2SO_4 concentration was lower than 1 g/L in the nanofiltration permeate and it could be recycled for brine refining stage avoiding the chromium pollution caused by subsequent treatment. The content of $Na_2Cr_2O_7$ in salt sludge was less than 8.5 ppm below the 10 ppm discharge standards. Then, the nanofiltration concentrate was frozen, Na_2SO_4 crystallized and precipitated. The supernatant mainly containing sodium dichromate could recycle to the electrolytic system. This method not only could recycle sodium dichromate, avoiding chrome sludge generated, but also could remove sulfate radicals.

Key words: Sodium chlorate, chrome sludge, nanofiltration, freezing crystallization, sodium dichromate recycling, sodium sulfate.

INTRODUCTION

Sodium chlorate used for preparing chlorine dioxide and a variety of chlorate salts is an important inorganic salt widely used in many areas, such as papermaking bleach, drinking water and wastewater treatment, printing and dyeing, medicine, pesticide, tanning, mineral processing (Bai, 2012). China sodium chlorate production capacity is about 200000 t/a, actual output of about 150000 t/a, equivalent to one or two factories' production capacity of the developed countries (Wang and Si, 2008). Domestic sodium chlorate production is still in the stage of development, and the scope of application is also constantly expanding, so the potential market is very broad. To save water resources, the crystallization mother liquor is returned to the process of dissolving salt and be recycled in the industrial production of sodium chlorate. However, compared with foreign countries, domestic existing brine purification equipment is relatively deficient, which leads to impurities such as sulfate radical abound,

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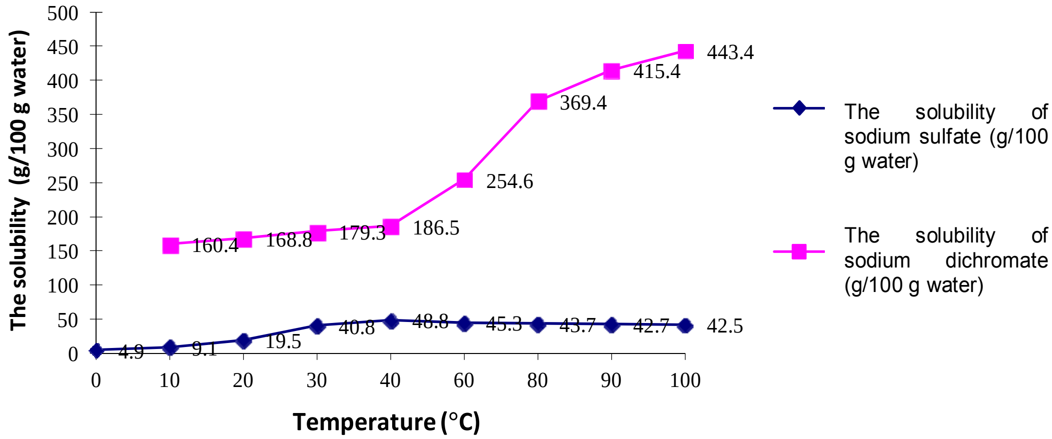

Figure 1. The solubility in the water of sodium dichromate and sodium sulfate.

and this will increase side reaction of the electrolytic process and reduce the current efficiency (Ye, 2008).

To avoid cathodic reduction reaction, it is necessary to add dichromate to electrolysis bath (Lin, 2006). In the existing process, chemical precipitations is often used to remove the sulfate radical in the crystallization mother liquor, which leads to the dichromate deposit to salt sludge together with sulfate, and finally causes chromium pollution (Gupta et al., 2002). Hexavalent chromium ion in dichromate will cause serious pollution to the environment and water source, thus do harm to fishing, forestry, agriculture and human health, and hexavalent chromium ion has a strong carcinogenic effect (Zhitkovich, 2011; Lone et al., 2013). Therefore, it is very urgent to solve the problem of chromium pollution in sodium chlorate production which has important theoretical significance and social value.

A series of processing for chrome sludge, landfill treatment, sludge deoxidation detoxification technology cannot achieve good results. The application of nano-material in containing Cr(VI) nanowastes processing achieves the effective separation of Cr(VI), recycling and nanowastes safe disposal (Liu et al., 2009). However, this method still cannot be applied on an industrial scale production and the processing cost is high.

At present, a variety of methods have been applied for the removal of Cr(VI) from industrial effluents which include chemical reduction-precipitation (Gheju and Balcu, 2011; Golder et al., 2007), adsorption (Cho et al., 2011), ion exchange (Lin and Kiang, 2003), membrane separation (Sankır et al., 2010; Ho and Poddar, 2001), biological reduction (Xu et al., 2009), radiolysis (Djouider, 2012), etc. The focus shifts from chrome sludge to the entire process of sodium chlorate production. So, we put forward the combination separation technology of nanofiltration and freezing crystallization for treating the crystallization mother liquor of sodium chlorate production in order to achieve the recycling utilization of sodium dichromate. It reduces costs, makes the wastewater and sludge produced in the production of sodium chlorate no longer contain chromium, and reaches safe discharge standards, so as to realize clean production. Furthermore, it achieves the purpose of separation sulfate ion from the system, and improves the efficiency of electrolysis.

MATERIALS AND METHODS

The separation of solutes by nanofiltration membranes results from a complex mechanism including steric hindrance as well as Donnan and dielectric effects (in the case of charged solutes) (Luo and Wan, 2013). It was reported that nanofiltration technology could separate low molecular weight solutes from inorganic salt solutions (Bao et al., 2013; Luo et al., 2009; Hong et al., 2006). Nanofiltration membranes have the advantages of providing a high water flux at low operating pressure and maintaining a high salt and organic matter rejection (Hilal et al., 2005; Moravia et al., 2013). In addition, the nanofiltration process benefits from easy operation, high reliability and relatively low energy consumption as well as high efficiency of pollutant removal, so it has become a very valuable water treatment in the field of separation technology nowadays. Some studies have shown that nanofiltration membrane technology could be successfully used in the treatment of wastewater containing chromium (Wang et al., 2007; Cassano et al., 2007; Campagna et al., 2013). At the same time, membrane separation technology is also applied to the separation of sulfate and chloride ions in the chlor-alkali industry and has achieved a satisfactory result (Xiao et al., 2009).

The solution separated in this process is the crystallization mother liquor of sodium chlorate production. The main anions of the solution are Cl^-, SO_4^{2-} and $Cr_2O_7^{2-}$. The Cl^- is monovalent monatomic anion, and its relative molecular weight is 35.45, while the SO_4^{2-} and $Cr_2O_7^{2-}$ are bivalent polyatomic anions and their relative molecular weight are 96.07 and 216.00, respectively. Compared with Cl^-, SO_4^{2-} and $Cr_2O_7^{2-}$ have a heavier weight, larger size, more number of charges, and the interception of nanofiltration membrane to SO_4^{2-} and $Cr_2O_7^{2-}$ is greater than that of Cl^- (Luo et al., 2009). Therefore, it is logical that choosing appropriate nanofiltration membrane to realize the interception and enrichment of SO_4^{2-} and $Cr_2O_7^{2-}$ and the purification of Cl^-.

As shown in Figure 1, compared with the sodium dichromate, the sodium sulfate has a low solubility in water, and with the decrease

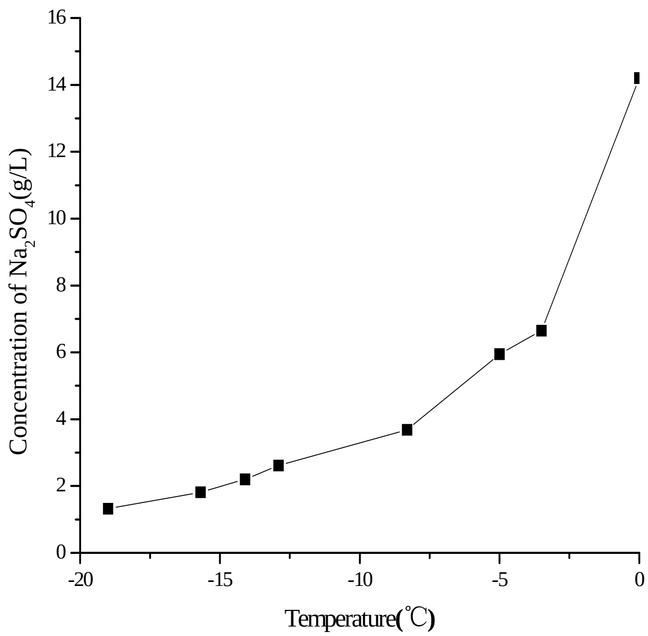

Figure 2. Sodium sulfate concentration changes with temperature during -20~0°C.

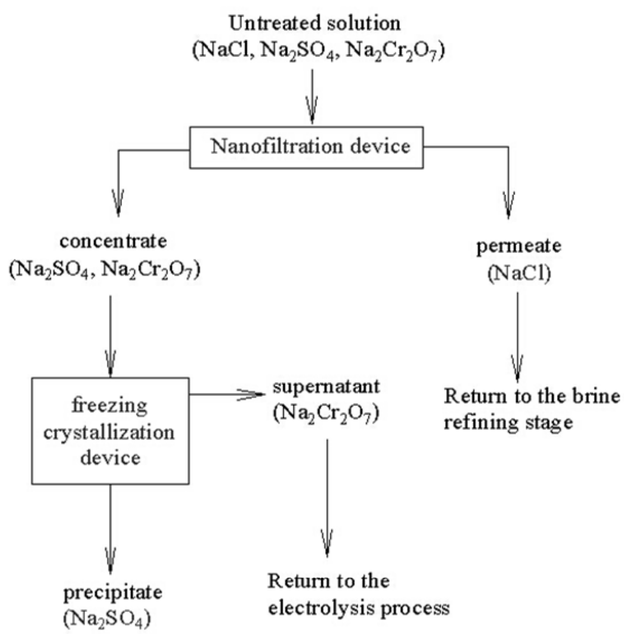

Figure 3. The process flow diagram.

of temperature, it will decline significantly. Especially under the condition of low temperature, the solubility of sodium sulfate is far lower than that of sodium dichromate. Figure 2 shows that in -8~0°C the reducing rate of sodium sulfate solubility is faster, but it becomes smooth below the temperature. Freezing crystallization temperature is controlled below -5°C, Na_2SO_4 concentration in the solution is less than 5 g/L after freezing (Cui, 2012). Combined with the energy saving consideration, the freezing crystallization temperature is generally determined as -5~-10°C. So, freezing crystallization method is effective by this way, the sodium dichromate can be concentrated under the low temperature, and sodium sulfate crystallize and separate out, realizing the separation of them.

In summary, nanofiltration device can realize the purification of Cl^- and the intercept and enrichment of SO_4^{2-} and $Cr_2O_7^{2-}$, and through freezing crystallization, SO_4^{2-} can crystallize and precipitate, while $Cr_2O_7^{2-}$ is recycled. Finally, the recycling of sodium dichromate in production of sodium chlorate will be realized at the same time the sulfate impurity is removed.

The main technological process includes nanofiltration separation and crystallization separation as shown in Figure 3. Experimental equipment mainly comprises raw material tank, pump, pressure gauge, nanofiltration device and freezing crystallization device as shown in Figure 4. Nanofiltration membrane used in the experiment was GE2540, volume type membrane, effective membrane area 2.5 m^2, salt rejection 98%, and the coat material is glass fiber reinforced plastic. CIC-100 ion chromatography was used for the analysis of negative ion concentration following the standard of HJ/T84-2001 "Water quality-determination of inorganic anions by ion chromatography".

The property parameters of the raw material liquid are shown in Table 1, and experimental operating conditions are shown in Table 2. The main ingredient of penetrating fluid through nanofiltration device was NaCl which can be returned directly to the brine refining stage. Concentrates mainly composed of Na_2SO_4 and $Na_2Cr_2O_7$ which need to be further separated by freezing crystallization. After crystallization by freezing, Na_2SO_4 precipitated from the solution, and $Na_2Cr_2O_7$ presented in the supernatant. The supernatant can be returned to sodium chlorate electrolysis system to inhibit side reactions, protecting the cathode electrode, so as to achieve the recycling of $Na_2Cr_2O_7$.

RESULTS

The experiment was repeated six times and the experimental dates were shown in Table 2. The $Na_2Cr_2O_7$ concentrations were all lower than 0.05 g/L, Na_2SO_4 concentrations were lower than 1 g/L in the nanofiltration permeate, and the permeate could be recycled for the brine refining stage. The content of $Na_2Cr_2O_7$ in salt sludge was less than 8.5 ppm.

DISCUSSION

The experimental results show that, the permeance of sodium chloride and concentration of sodium sulfate and sodium dichromate could be effectively achieved by using nanofiltration. The raw material liquid contains NaCl, Na_2SO_4 and $Na_2Cr_2O_7$, membrane to the interception of SO_4^{2-} and $Cr_2O_7^{2-}$ is prior to Cl^-. If the concentration of Na_2SO_4 and $Na_2Cr_2O_7$ increases, membrane for interception of Cl^- rate reduces. In order to maintain neutral through the membrane of sodium ions will also increase. When the multivalent ions concentration reaches certain value, the retention rate of monovalent ions even can appear negative, namely the Cl^- concentration in permeate is greater than that of the feed.

In the six groups of repeated experiments, $Na_2Cr_2O_7$ concentrations were all lower than 0.05 g/L, Na_2SO_4

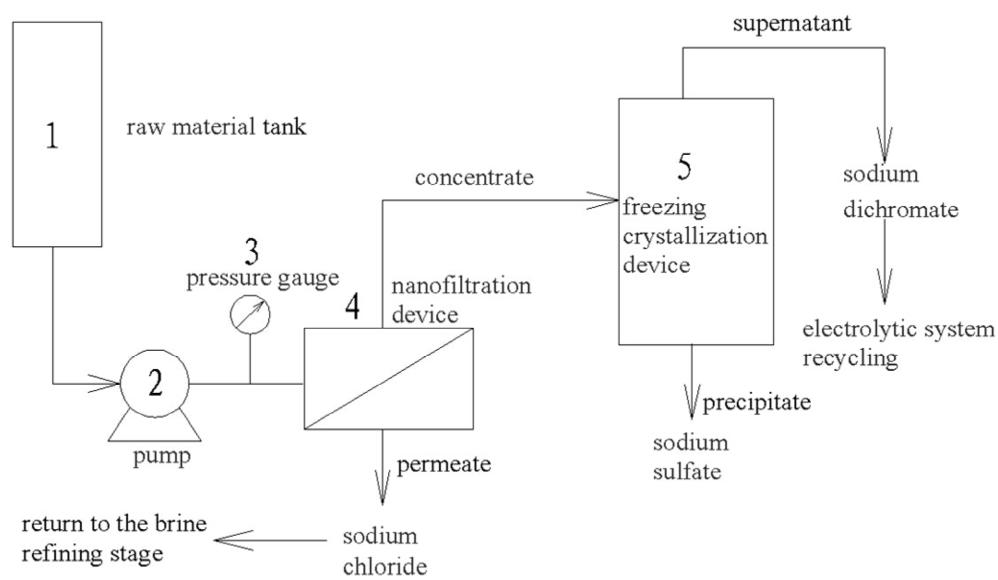

Figure 4. The process flow diagram for the sodium dichromate recycling and sulfate radical removal in the crystallization mother liquor.

Table 1. The property parameters of the raw material liquid.

Concentration (g/L)			Volume (L)	pH
NaCl	Na_2SO_4	$Na_2Cr_2O_7$		
113	29	3.35	40	8.59 - 9.5

Table 2. The experimental operating conditions.

NF inlet pressure (MPa)	NF flow rate (L/min)	Freezing crystallization temperature (°C)	The temperature of raw material solution (°C)
0.5 to 1.5	20	-5 ~ -10	25

concentrations were lower than 1 g/L in the nanofiltration penetrating fluid, and the penetrating fluid could be recycled for the brine refining stage. The content of $Na_2Cr_2O_7$ in salt sludge was less than 8.5 ppm, lower than the United States environmental protection agency of hexavalent chromium content in the sludge discharge standard 10 ppm. Then, the nanofiltration concentrate was frozen, Na_2SO_4 crystallization precipitation, and supernatant could recycle to the electrolytic system. This method not only could recover sodium dichromate but also remove sulfate radicals.

Conclusions

The nanofiltration permeate could be recycled to the brine refining stage, $Na_2Cr_2O_7$ concentration was lower than 0.05 g/L to avoid the subsequent processing of chromium pollution. The $Na_2Cr_2O_7$ content in salt sludge was less than 8.5 ppm below the United States environmental protection agency on the discharge standard of hexavalent chromium content in sludge 10 ppm. Na_2SO_4 concentration in permeate was lower than 1 g/L, which could meet the production requirements. The nanofiltration concentrate was frozen, Na_2SO_4 crystallized and precipitated, and the supernatant was recycled to the electrolytic system, which not only could recover sodium dichromate but also remove sulfate radicals.

This process effectively realized sodium dichromate recycling in the production of sodium chlorate, at the same time also removed sulfate radicals, and solved the dichromate pollution in salt sludge from the original precipitation process.

Conflict of Interests

The author(s) have not declared any conflict of interests.

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