Kinetics and mechanism of desilication reaction in sodium chromate solution using sodium aluminate

Jianxin Chen, Xiangchao Zhang, Jian Han, Yinhui Li, Min Su and Aidang Lu

ABSTRACT

It is essential to control silica levels in sodium chromate solution during the process of electrolytic synthesis of sodium dichromate. On the basis of previous work, the desilication conditions were systematically studied and pH was found to have the most serious impact on the desilication process. The desilication rate under optimal conditions obtained from the orthogonal experiment results was up to 99.3%. Kinetic experiments showed that the desilication reaction was first-order in SiO2 concentration and the apparent activation energy was calculated to be 22 kJ mol⁻¹, which is far less than the reported values. The morphology and structure of the desilication reaction product (DSP) were studied by scanning electron microscope (SEM) and X-ray diffraction (XRD). SEM showed that DSP had a loose etched structure. The pattern of XRD illustrated the crystallinity of DSP increased along the duration of the experiment. The phase of DSP was mainly Na₆(AlSiO₄)₆. Based on the experimental data, the desilication mechanism has been discussed. The hexameric aluminosilicate ions were produced by the reaction of monomeric aluminosilicate ion, through hydrogen bond interaction, which was formed by SiO₂(OH)₂⁻ and Al(OH)₃.

Key words | desilication, electrolytic synthesis, mechanism, reaction kinetics, sodium aluminate, sodium chromate

INTRODUCTION

As an important chemical raw material widely used in many fields, sodium dichromate is a precursor of many chromium compounds (Wang et al. 2015), but the traditional chromic salts industry is facing a serious challenge because of its substantial environmental pollution. Compared with sulfuric acid methods and carbonization methods, the electrochemical synthesis process of chromate production has attracted greater attention as a green technology and is still in the development stage (Ahmed et al. 2001). It not only solves environmental pollution problems in the production of chromate, but also produces sodium hydroxide, hydrogen and oxygen by-products which have high economic value. The compounds of silicon and aluminium are the main impurities in the sodium chromate solution. Silicate ions react with other ions in the sodium chromate solution to form precipitation as desilication reaction products (DSPs). In the electrolysis procedure, DSP can deposit as scale on the electrolytic tank, affecting the continuous operation of the electrolytic process and the quality of the products, decreasing electrolysis efficiency. Therefore, only the removal of silicates from sodium chromate solution before the electrolysis stage can ensure the smooth progress of the entire follow-up process.

Chemical treatment (primary precipitation) is considered as a suitable method valuable to wastewater treatment (Indah et al. 2016). The removal of silicates from solution is mostly achieved by introducing chemicals which can react with silicate ions to produce insoluble compounds. At present, high capacity desilication agents that have been reported most are calcium compounds, including CaO (Zhao et al. 2002), Ca(OH)₂ (Gu et al. 2002), 3CaO·Al₂O₃·6H₂O (Yuan & Zhang 2009), CaSO₄·2H₂O (Ma et al. 2011), Friedel’s salt (Ma et al. 2009), etc. However, the reaction between sodium chromate and calcium ion will form the carcinogen of calcium chromate (Reyes-Gutiérrez & Rodríguez-Castillo 2009). Therefore, adding calcium salt for desilication is not applied for sodium chromate solution. Iron salts also can be used to remove the silicate (Jolsterá et al. 2010), which is expensive. There are two other methods of desilication: increasing the...
alkalinity (Groen et al. 2007a, 2007b; Jin et al. 2009) and increasing the temperature of the solution (Ma et al. 2009). However, it is difficult to adjust the pH value for the high alkali concentration in raw liquor of sodium chromate, so both methods are difficult to apply or are insufficient for treating the raw liquor.

The desilication kinetics and mechanism have been extensively studied. For example, the desilication kinetics of adding Ca(OH)₂ has been proposed, such as the extensively studied. For example, the desilication kinetics of treating the raw liquor. However, it is difficult to apply or are insufficient for treating the raw liquor.

MATERIALS AND METHODS

Experimental materials and apparatus

The chemicals Na₂CrO₄·4H₂O, Na₂SiO₃·9H₂O, NaAlO₂, NaOH and HCl were of analytical grade from Sinopharm Chemical Reagent Co., Ltd (Beijing). All experimental water was distilled water (conductivity <0.1 μS cm⁻¹). All chemical reagents were used without further purification.

Silicate-containing sodium chromate solution preparation

Silicate-containing sodium chromate solution was prepared by dissolving Na₂CrO₄·4H₂O and Na₂SiO₃·9H₂O in distilled water. Silicate-containing sodium chromate solution was composed of 275 g L⁻¹ Na₂CrO₄ and 109 mg L⁻¹ SiO₂, which was made up to reflect the composition of actual production (Sun et al. 2002; Guo et al. 2011; Liu et al. 2012).

Desilication experiments

The desilication test was conducted in a 200 mL double-layer glass reactor which was heated by circulating water. The temperature was controlled within the set point of ±0.5 °C. Water was heated in a thermostated bath. When the temperature of the solution reached the reaction value, a certain amount of sodium aluminate was introduced. Samples were collected at intervals.

Analysis methods

After cooling, the resulting solution was filtered with 0.45 μm filter paper, the silicon concentration in the solution was determined by inductively coupled plasma emission spectroscopy (5300dv ICP-AES) and expressed as C_SiO₂. DSP was filtered, washed and then dried for X-ray diffraction (XRD) (Bruker D8 Advanced XRD diffractometer) and scanning electron microscope (SEM) (Nova NanoSEM 450) analysis. XRD patterns were recorded in the range of 5–90° (using Cu Kα radiation).

RESULTS AND DISCUSSION

Desilication tests in silicate-containing sodium chromate solution

It is necessary to develop simple and effective methods to remove silicates from sodium chromate solution in order to avoid deleterious impacts on human health. Here we report an efficient strategy to remove silicates from sodium chromate solution by using sodium aluminate as precipitant (Figure 1). The removal efficiency of the chemical precipitation method is dependent on many parameters, such as pH, reaction time, and reaction temperature. Therefore, the effects of desilication temperature, desilication time, Al/Si and pH value on the desilication effect have been studied through a set of orthogonal experiments. On the basis of the experimental results, the reaction kinetics and mechanism are presented.
Orthogonal test of desilication reaction

Results of the orthogonal test, presented as the average values of three replicates, are shown in Table 1 (the coefficients of variation were <5% in all cases). From the results of the orthogonal experiment it can be deduced that the influence of the four parameters on the desilication rate is obviously different and the desilication process was highly pH dependent. However, the parameter of pH is not presented in previous work. There are two main reasons for this result. (1) Sodium aluminate undergoes hydrolysis reactions in water. These reactions can lead to the formation of monomers or multinuclear species, depending on solution pH (Barany et al. 2006). (2) The reduction of pH can inhibit the polymerization of aluminium ions and silicate ions, thereby affecting the desilication rate (Wu et al. 2008). The results show that the optimized conditions are as follows: the desilication temperature is 303 K, the desilication time is 4 min, Al/Si is 4:1 and the pH value is 8. Under optimal conditions, the desilication rate is up to 99.3%.

Table 1 | Results of the orthogonal experiments

<table>
<thead>
<tr>
<th>Test number</th>
<th>Al/Si</th>
<th>T (K)</th>
<th>t (min)</th>
<th>pH</th>
<th>Desiliconization rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2:1</td>
<td>303</td>
<td>12</td>
<td>8</td>
<td>96.16</td>
</tr>
<tr>
<td>2</td>
<td>2:1</td>
<td>323</td>
<td>8</td>
<td>11</td>
<td>88.10</td>
</tr>
<tr>
<td>3</td>
<td>2:1</td>
<td>343</td>
<td>4</td>
<td>9.5</td>
<td>92.04</td>
</tr>
<tr>
<td>4</td>
<td>1:1</td>
<td>303</td>
<td>8</td>
<td>9.5</td>
<td>91.76</td>
</tr>
<tr>
<td>5</td>
<td>1:1</td>
<td>323</td>
<td>4</td>
<td>8</td>
<td>96.89</td>
</tr>
<tr>
<td>6</td>
<td>1:1</td>
<td>343</td>
<td>12</td>
<td>11</td>
<td>86.27</td>
</tr>
<tr>
<td>7</td>
<td>4:1</td>
<td>303</td>
<td>4</td>
<td>11</td>
<td>90.25</td>
</tr>
<tr>
<td>8</td>
<td>4:1</td>
<td>323</td>
<td>12</td>
<td>9.5</td>
<td>92.83</td>
</tr>
<tr>
<td>9</td>
<td>4:1</td>
<td>343</td>
<td>8</td>
<td>8</td>
<td>97.90</td>
</tr>
</tbody>
</table>

K1j/% | 276.30 278.18 275.26 290.94
K2j/% | 274.93 277.82 277.76 264.63
K3j/% | 280.98 276.21 279.18 276.63
M1j/% | 92.10 92.73 91.75 96.98
M2j/% | 91.64 92.61 92.59 88.21
M3j/% | 93.66 92.07 93.06 92.21
Rj/% | 2.02 0.66 1.31 8.77

Kinetics of desilication reaction

Figure 2 shows plots of the SiO2 concentration as a function of desilication time and desilication temperature for solutions initially containing 109 mg L⁻¹ SiO2. As seen in Figure 2(a),...
temperature has an insignificant influence on both the rate and extent of desilication. The desilication rate increased rapidly and then rather slowly with prolonged time. Even in different temperatures, >92% silica in sodium chromate solution could be removed. At the same time, it can be seen that the desilication process was finished within 10 min. The aluminosilicate has definite adsorptive properties, which enable it to quicken the reaction rate and improve the desilication rate (Abdel-Wahab & Batchelor 2001).

The desilication kinetics can be quantified by a power law relationship of the form (Cousineau & Fulford 1987):

\[ \frac{dC}{dt} = k C^n \]  

(1)

where \( C \) is the SiO\(_2\) concentration (g L\(^{-1}\)) at any time; \( t \) is desilication time (min); \( k \) is desilication rate constant (min\(^{-1}\)); \( n \) is the order of the desilication reaction.

Figure 2(b) shows plots of \( \ln(C_0/CSiO_2) \) against time, where \( C_0 \) and \( CSiO_2 \) are the initial and anytime SiO\(_2\) concentration. Figure 2(b) presents a good linear relation for each temperature, with a correlation coefficient (\( R^2 \)) of above 0.996 (Table 2), which indicates the desilication reaction is first-order in SiO\(_2\) concentration. According to Equation (1), the kinetic equation of the desilication reaction can be written as:

\[ \ln\left(\frac{C_0}{CSiO_2}\right) = kt \]  

(2)

The relationship between desilication temperature and the desilication constant \( k \) obtained from Equation (2) can be expressed by the Arrhenius equation:

\[ k = A \exp\left(-\frac{E_a}{RT}\right) \]  

(3)

where \( k \) is the overall rate constant; \( A \) is the frequency factor; \( E_a \) is the apparent activation energy; \( R \) is the ideal gas constant; and \( T \) is the desilication temperature.

Table 2 | Square of the correlation coefficient (\( R^2 \)) and desilication rate constants (\( k \)) at various temperatures

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>( R^2 )</th>
<th>( k ) (min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>338</td>
<td>0.9962</td>
<td>0.2845</td>
</tr>
<tr>
<td>348</td>
<td>0.9972</td>
<td>0.3452</td>
</tr>
<tr>
<td>358</td>
<td>0.9969</td>
<td>0.4452</td>
</tr>
<tr>
<td>368</td>
<td>0.9982</td>
<td>0.5271</td>
</tr>
</tbody>
</table>

Plotting the values of \( \ln k \) obtained at different desilication temperatures against 1,000/\( T \) fit reasonably to a straight line with a correlation coefficient of 0.993 (Figure 3). From the slope of this plot, the apparent activation energy of the desilication of the sodium chromate solution by sodium aluminate was calculated to be 22 kJ mol\(^{-1}\). This value is much smaller compared to that for general chemical reactions (60–250 kJ mol\(^{-1}\)) (Table 3) (Li et al. 2007). This shows that the desilication reaction from sodium chromate solution using sodium aluminate overcomes a lower potential barrier and has a larger potential for future development.

The morphologies of sodium aluminate and DSP

The sodium aluminate and DSP were examined using a SEM. The typical SEM images are presented in Figure 4. It can be clearly seen that the solid phase (NaAlO\(_2\)) is columnar aggregate, while the solid phase (DSP) has a loose etched structure. The DSP was analyzed by using SEM and XRD and was formed at 358 K with a stirring

Table 3 | The activation energy values compared with the reported papers

<table>
<thead>
<tr>
<th>Desilication additives</th>
<th>Activation energy (kJ mol(^{-1}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>3CaO·Al(_2)O(_2)·6H(_2)O</td>
<td>96</td>
<td>Yuan &amp; Zhang (2009)</td>
</tr>
<tr>
<td>CaSO(_4)·2H(_2)O</td>
<td>52</td>
<td>Ma et al. (2011)</td>
</tr>
<tr>
<td>Friedel’s salt</td>
<td>57.7</td>
<td>Ma et al. (2009)</td>
</tr>
<tr>
<td>Ca(OH)(_2)</td>
<td>117</td>
<td>Gu et al. (2002)</td>
</tr>
<tr>
<td>NaAlO(_2)</td>
<td>22</td>
<td>This work</td>
</tr>
</tbody>
</table>
speed of 100 rpm and Al/Si = 1:1. Incidentally, the loose structure was in step with the adsorptive properties of sodium aluminosilicate mentioned above.

The XRD characterizations of DSP

Figure 5(a) shows that the DSP does not form a stable crystal structure at the beginning. Then, as the reaction progresses, it can be seen from Figure 5(b) that sodium aluminate crystals gradually formed. After a reaction time of 60 min, the product showed several diffraction peaks and that crystallinity improved with prolonged time (Figure 5(c)). The sodium aluminosilicate was mainly amorphous at the beginning and the large crystal cell needed more time to change into better crystal form (Radomirovic et al. 2015). This is also because the stability of crystalline phase DSP is larger than that of the amorphous phase (Pan et al. 2016). The XRD results suggested that the major phases in the DSP were \( \text{Na}_6(\text{AlSiO}_4)_6 \) (JCPDS 42-0217).

Sodium aluminosilicate contains many phases such as amorphous sodium aluminosilicate, sodalite, and cancrinite (Jolivet et al. 2011). The molecular formula of DSP is similar to natural silicate minerals, such as sodalite \( \text{Na}_4(\text{Al}_3\text{Si}_3\text{O}_{12})\text{Cl} \), nepheline \( \text{KNa}_3(\text{AlSiO}_4)_4 \) and hydroxysodalite \( \text{Na}_6\text{Al}_3\text{Si}_6\text{O}_{24}(\text{OH})_2 \), which can expressed by the empirical formula \( Z_x(\text{AlSiO}_4)y\cdot m\text{Y} \), where \( Z \) is a cation such as potassium or sodium, \( X \) is degree of polycondensation, \( m \) can be zero, and \( Y \) represents a variety of inorganic anions, such as Cl\(^-\) and OH\(^-\).
The mechanism of desilication reaction

Based on experiment data and related literature, the desilication mechanism by adding sodium aluminate can be described as follows. The monomeric silicate anion, namely $\text{H}_2\text{SiO}_3^-$, is the predominant species in the sodium chromate solution due to the low silicon concentration and high alkalinity (Zeng & Li 2012). It should be noted that, at the alkaline pH, the predominant Al(III) species is $\text{Al(OH)}_4^-$ (Li et al. 2004), due to the hydrolysis reaction to aluminate (Tiravanti et al. 1997):

$$\text{Al(OH)}_4^- \leftrightarrow \text{AlO}_2^- + \text{H}_2\text{O} \quad (4)$$

The equation for the overall reaction may be written as (Li et al. 2002; Vadim 2016):

$$\text{H}_2\text{SiO}_3^- \leftrightarrow \text{SiO}_2(\text{OH})_2^{2-} \quad (5)$$

$$6\text{Na}^+ + 6\text{Al(OH)}_4^- + 6\text{SiO}_2(\text{OH})_2^{2-} \rightarrow \text{Na}_6(\text{AlSiO}_4)_6 + 12\text{OH}^- + 12\text{H}_2\text{O} \quad (6)$$

At the beginning, the monomeric aluminosilicate ion was formed by the reaction of $\text{SiO}_2(\text{OH})_2^{2-}$ and $\text{Al(OH)}_4^-$. In this process, the Al-O-Al bond was replaced by an Al-O-Si bond because the silicon atom radius is larger than an aluminum atom, and the Al-O-Si bond is more stable than the Al-O-Al bond (Wang et al. 2003). The hydrogen bonds between Al-O-Si and OH bonds are stronger than the Al-O-Al bond because the silicon atom radius is larger than an aluminum atom, and the Al-O-Si bond is more stable than the Al-O-Al bond (Wang et al. 2003). The hydrogen bonds between Al-O-Si and OH bonds are stronger than the Al-O-Al bond, which causes the production of hexameric aluminosilicate ion. Finally, the DSP was generated by the reaction of hexameric aluminosilicate ions and sodium ions. The existence of the hexameric aluminosilicate also made the desilication reaction complete quickly.

CONCLUSIONS

Orthogonal experimental results showed the effects of various factors on the desilication rate: pH $>$ Al/Si $>$ reaction temperature $>$ reaction time. The results suggested that the optimized conditions in this work were as follows: 4 min reaction time, 4:1 Al/Si, reaction temperature at 303 K, pH 8. The optimal condition for the removal of silicon is 99.3%. Kinetics results showed that the desilication reaction is a first-order reaction and the apparent activation energy is 22 kJ mol$^{-1}$. The characterization of SEM results showed that the sodium aluminate and DSP had a columnar and a loose etched structure, respectively. The XRD results suggested that the product was mainly Na$_6$(AlSiO$_4$)$_6$, and the crystallinity improved with increasing reaction time. The process of removing silicon is as follows: at first, $\text{SiO}_2(\text{OH})_2^{2-}$ and $\text{Al(OH)}_4^-$ formed monomeric aluminosilicate ion; then, the DSP was produced by the reaction of sodium ion and hexameric aluminosilicate ion which was formed by monomeric aluminosilicate ion through hydrogen bond interaction.

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