Study on causticizing process of sewage discharged from wet reclamation of waste sodium silicate sand

Lichi Wang¹, Wenming Jiang¹ and Zitian Fan¹, a

¹State Key Lab of Materials Processing and Die & Mould Technology, Huazhong University of Science and Technology, Wuhan; 430074, PR China

a Corresponding author: fanzt@hust.edu.cn

Abstract. Wet reclamation of waste sodium silicate sand produces a large amount of alkaline sewage and causes secondary pollution. At present, the neutralization method is commonly used to treat the sewage discharged from the wet reclamation. However, treated sewage contains a large amount of soluble salts, and still causes environmental problems directly discharged. The main solutes in the sewage discharged from the wet reclamation are sodium carbonate and sodium bicarbonate, so the sewage can be converted into lye by a causticizing process and be recycled. In this paper, the causticizing process of the sewage discharged from the wet reclamation was studied, and the effects of causticizing temperature, causticizing time, quicklime consumption, and sewage concentration on causticization rate were investigated. The results showed that it was feasible to treat the sewage discharged from the wet reclamation through the causticizing process, and the causticization rate could be above 92%. Increasing the causticizing temperature, prolonging the causticizing time, improving the quicklime consumption, and reducing the sewage concentration could improve the causticization rate.

1. Introduction

The sodium silicate sand casting has been widely used in Chinese foundries due to its advantages including low cost, non-toxic, odorless, and good casting quality [1-2]. In China, millions of tons of waste sodium silicate sand are produced every year, causing serious environmental problems. In 2013, Chinese government promulgated the “Entry Conditions for the Foundry Industry”, which required the reuse rate of the waste sodium silicate sand to be no less than 60%. The waste sodium silicate sand has to be reclaimed before it is reused. At present, the main methods of reclaiming the waste sodium silicate sand are dry reclamation and wet reclamation [1-6]. The dry reclamation is simple and low-cost, but the reclaimed sand is of poor quality and cannot replace new sand directly. The reclaimed sand obtained by the wet reclamation is of good quality and can replace new sand directly. However, the wet reclamation produces a large amount of alkaline sewage and causes secondary pollution [7]. If the problem of sewage treatment were solved, the wet reclamation would become an environmentally friendly way to reclaim the waste sodium silicate sand.

At present, the treatment process of the sewage discharged from the wet reclamation includes neutralizing by adding acid, and precipitating or filtering [8-9]. Although the treated sewage is not alkaline, it contains a large amount of soluble salts, and will cause environmental problems if it is directly discharged [10-13]. The main solutes in the sewage discharged from the wet reclamation are sodium carbonate and sodium bicarbonate, which means the sewage can be converted into lye by a causticizing process [14-16] and be recycled. Recycling sewage can avoid environmental problems and generate economic benefits. However, as water consumption of the wet reclamation is high, the
concentration of the sewage discharged from a single wet reclamation is not high enough for recycling. Reusing sewage can improve the concentration of the sewage. Reusing sewage means the sewage discharged from the wet reclamation of a batch of the waste sodium silicate sand is filtered, and then directly used instead of fresh water in the wet reclamation of another batch of the waste sodium silicate sand. The high-concentration sewage obtained after reusing sewage can be converted into lye by the causticizing process, and the lye can be used to produce water glass. The CaCO3 produced during the causticizing process can be decomposed into quicklime for the causticizing process after calcination.

In this paper, the causticizing process of the high-concentration reused sewage discharged from the wet reclamation was studied, and the effects of causticizing temperature, causticizing time, quicklime consumption, and sewage concentration on causticization rate were investigated.

2.Materials and methods

2.1 Experimental materials
The sewage used in the experiments was the sewage discharged from the wet reclamation of the waste sodium silicate sand hardened with carbon dioxide, and the sewage had been reused several times. The more times the sewage were reused, the higher the concentration of the sewage was. The sewage had been filtered with filter membranes with a mean pore diameter of 5 µm before the causticizing process. The main components of the filtered sewage are shown in Table 1. Quicklime powder was used instead of lime milk so that the lye concentration would not decrease. The CaO content of the quicklime powder was 95%. The other reagents used were of analytical reagent grade, and the water used was deionized water.

| Reuse times | Na2CO3 (g/L) | NaHCO3 (g/L) |
|-------------|--------------|--------------|
| 3           | 92.9         | 31.7         |
| 4           | 112.9        | 38.5         |
| 5           | 122.9        | 41.9         |

2.2 Causticizing process
The sewage (100.0 mL) was put into a beaker and then heated to a certain temperature in a water bath. Then a certain amount of the quicklime powder was added into the beaker and the mixture was stirred for a period of time. At last the beaker was removed from the water bath and let stand until the lye was clarified.

2.3 Analysis
The clear lye was titrated with phenolphthalein and methyl orange as indicators to measure the normality of NaOH and Na2CO3, and the effect of the causticizing process was evaluated by the causticization rate. The causticization rate was calculated as follow.

\[
\text{Causticization rate} = \frac{N_{\text{NaOH}}}{N_{\text{NaOH}}+N_{\text{Na2CO3}}} \quad (1)
\]

where \(N_{\text{NaOH}}\) was the normality of NaOH and \(N_{\text{Na2CO3}}\) was the normality of Na2CO3 in the clear lye.

3.Results and discussion

3.1 Effect of causticizing temperature on the causticization rate
The sewage used in the experiments had been reused 3 times. The ratio of the amount of CaO in the quicklime powder to the theoretical demand \((n_{\text{CaO}})/(n_{\text{Na2CO3}}+n_{\text{NaHCO3}})\) was 1.2:1, and the mixture was stirred for 15 min. As shown in Fig. 1, when the causticizing temperature is 60°C, the causticization rate is below 50%; the causticization rate will be about 90% when the causticizing temperature is no less than 70°C. After the quicklime powder is added into the sewage, CaO reacts with water and forms Ca(OH)2 (digestion reaction), and the higher the causticizing temperature is, the faster the digestion
reaction is. Then Ca(OH)$_2$ reacts with Na$_2$CO$_3$ and NaHCO$_3$ in the sewage and forms CaCO$_3$ (causticization reaction) with low solubility. When the causticizing temperature is low, the digestion reaction is slow, and the CaCO$_3$ precipitate formed during the causticization reaction covers the surfaces of the quicklime powder and stops the digestion reaction. So the digestion reaction is not thorough and the causticization rate is low in the lack of Ca(OH)$_2$. When the causticizing temperature is high, the digestion reaction is fast, and the CaCO$_3$ precipitate cannot cover as many as the surfaces of the quicklime powder in time. So the digestion reaction is relatively thorough and the causticization rate is high. Since the causticization reaction is reversible and cannot be thorough even with excessive Ca(OH)$_2$, the causticization rate cannot reach 100%.

Figure 1. Effect of causticizing temperature on the causticization rate.

3.2 Effect of causticizing time on the causticization rate

The sewage used had been reused 3 times and the $n_{(CaO)}:n_{(Na_2CO_3+NaHCO_3)}$ was 1.2:1. As shown in Fig. 2, when the causticizing temperature is 90°C, the causticization rate rises rapidly to 92.2% in the first 3 min, and then remains basically unchanged, indicating that the causticizing process can be completed in 3 min at 90°C. When the reaction is carried out at 80°C, the causticization rate rapidly increases to 82.8% in the first 3 min, and then continues to rise and reaches 89.4% in 8 min, indicating that the causticizing process takes a relatively long time to be complete at 80°C. Therefore, the causticization time should be 3 min and the causticizing temperature should be 90°C.

Figure 2. Effect of causticizing time on the causticization rate.

3.3 Effect of quicklime consumption on the causticization rate
The sewage used had been reused 3 times. As shown in Fig. 3, when the amount of CaO in the quicklime powder equals to the theoretical demand, the causticization rate is only 81.1%. This is because the digestion reaction cannot be thorough in the sewage, so Ca(OH)\textsubscript{2} is insufficient for the causticization reaction. As the quicklime consumption increases, the amount of Ca(OH)\textsubscript{2} involved in the causticization reaction also increases, causing an increase in the causticization rate. The ratio of the amount of CaO in the quicklime powder to the theoretical demand should be 1.2:1, so that the causticization rate can be high while the amount of CaCO\textsubscript{3} involved in the calcination process is not large.

![Figure 3. Effect of quicklime consumption on the causticization rate.](image)

3.4 Effect of sewage concentration on the causticization rate

As shown in Fig. 4, with the increase of the sewage concentration, the causticization rate decreases from 92.2% to 87.6%. In the causticization reaction, the stoichiometric number of NaOH is greater than the stoichiometric number of Na\textsubscript{2}CO\textsubscript{3}, so the increase in the concentration of the sewage has a greater influence on the right side of the equation, causing the equilibrium to move to the left, resulting in a decrease in the causticization rate.

![Figure 4. Effect of sewage concentration on the causticization rate.](image)

3.5 Orthogonal experiment analysis

The effect degrees of the causticizing temperature, the causticizing time, the quicklime consumption, and the sewage concentration on the causticization rate should be investigated, so an orthogonal experiment of four factors and three levels was performed. The results and analysis of the orthogonal experiment are shown in Table 2 and Fig. 5. The descending order of the factors by effects on the
Causticization rate is the causticizing temperature, the sewage concentration, the quicklime consumption, and the causticizing time. Increasing the causticizing temperature, prolonging the causticizing time, improving the quicklime consumption, and reducing the sewage concentration can improve the causticization rate. Under the experimental conditions, the causticization rate has a maximum value of 92.7% when the reuse times of the sewage are 3, the causticizing temperature is 90°C, the quicklime consumption is 1.20 times of the theoretical demand, and the causticizing time is 7 min. Since the causticizing process can be completed in 3 min at 90°C, the causticizing time should be 3 min to save time.

![Figure 5. Effect of sewage concentration, temperature, quicklime consumption, and time on the causticization rate.](image)

| Number | Reuse times | Temperature (ºC) | Quicklime consumption | Time (min) | Causticization rate (%) |
|--------|-------------|------------------|-----------------------|------------|------------------------|
| 1      | 5           | 80               | 1.10                  | 3          | 56.8                   |
| 2      | 5           | 85               | 1.15                  | 5          | 86.8                   |
| 3      | 5           | 90               | 1.20                  | 7          | 89.0                   |
| 4      | 4           | 80               | 1.15                  | 7          | 81.6                   |
| 5      | 4           | 85               | 1.20                  | 3          | 89.3                   |
| 6      | 4           | 90               | 1.10                  | 5          | 88.0                   |
| 7      | 3           | 80               | 1.20                  | 5          | 85.4                   |
| 8      | 3           | 85               | 1.10                  | 7          | 90.0                   |
| 9      | 3           | 90               | 1.15                  | 3          | 91.7                   |
| k1     |             |                  |                       |            | 77.5                   |
| k2     |             |                  |                       |            | 74.6                   |
| k3     |             |                  |                       |            | 78.3                   |
| R      |             |                  |                       |            | 79.3                   |
|        |             |                  |                       |            | 86.3                   |
|        |             |                  |                       |            | 88.7                   |
|        |             |                  |                       |            | 86.7                   |
|        |             |                  |                       |            | 86.7                   |
|        |             |                  |                       |            | 87.9                   |
|        |             |                  |                       |            | 86.9                   |
|        |             |                  |                       |            | 9.6                    |
|        |             |                  |                       |            | 7.6                    |

4. Conclusions
The main solutes in the sewage discharged from the wet reclamation of the waste sodium silicate sand hardened with carbon dioxide are sodium carbonate and sodium bicarbonate. Reusing sewage can improve the concentration of the sewage, and the high-concentration sewage can be converted into lye by the causticizing process. Quicklime powder should be used instead of lime milk, so that the lye concentration will not decrease. Increasing the causticizing temperature, prolonging the causticizing time, improving the quicklime consumption, and reducing the sewage concentration can improve the causticization rate. The causticization rate is 92.2% when the reuse times of the sewage are 3, the causticizing temperature is 90°C, the quicklime consumption is 1.20 times of the theoretical demand, and the causticizing time is 3 min.

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