

High-temperature reduction of chromium (VI) in solid alkali

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Abstract

Chromium (VI) that exists in many industrial wastes is considered highly toxic. One of the most common ways to dispose of these wastes is to reduce chromium (VI) to chromium (III), which is less toxic and can be relatively easily removed or fixed. However, the reduction of chromium (VI) is often conducted in acidic solutions and the chromium (VI) in alkaline solid wastes is hardly to be fully removed. The present study describes a new method for reducing chromium (VI) in alkaline solid. By mixing alkaline solids containing chromium (VI) with an aqueous sucrose solution and then calcinating the resulting mixture at 400–600 °C in inertial gas, chromium (VI) can be easily reduced to an insoluble chromium oxide. The reduced fraction can reach up to 99% in 10–20 min under the conditions of temperature above 600 °C and sucrose/chromium (VI) ≥ 1 g/1 g.

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1. Introduction

Chromium usually occurs in its compounds in the form of chromium (VI) or chromium (III), which are the most stable and common oxidation states of chromium. Compounds of chromium (VI) and chromium (III) have different solubilities and toxicities [1]. Chromium (III) is essential to animals and human beings. It is recommended that a daily uptake of 50–100 mg is helpful for human beings, without toxic effects observed even at a higher dosage [2]. In contrast, chromium (VI) has been proven highly toxic, and some chromates are considered as carcinogens [3]. Unfortunately, a large amount of chromium (VI)-containing wastes arise every day from tanning, electroplating, wood preservatizing, dyeing and production of chromium chemicals. Therefore, many countries have adopted severe restrictions on disposals of those industrial wastes. Quite a few methods for the removal of chromium (VI) have been studied, such as biosorption, ion exchange, solvent extraction, nanofiltration, micelle-enhanced ultra filtration, adsorption with inorganic sorbent materials, reduction and precipitation [4]. Among them, the most commonly used is reduction and pre-

cipitation. A number of chemical reductants for converting chromium (VI) to chromium (III) are described in patents [5,6] and literatures [7–15], including ferrous [Fe(II)] compounds, hydrogen peroxide, reductive sulfur compounds, hydrazines, hydroxylamines, formaldehyde, etc. However, almost all these reductants are used in aqueous solutions and most of them are in acidic solutions except for [Fe(II)], hydrazines and hydroxylamines. Few reports have been found involving in the reduction of chromium (VI) in solid wastes, especially in alkaline solids. Pohlantdt-Schwandt et al. [2,16] studied the reduction and removal of chromium (VI) in alkaline wood ash by water leaching and formaldehyde reduction. The present study provides a new method for reducing chromium (VI) in solid sodium bicarbonate with sucrose, starch or flour used as reductants. This method is promised to be applied to the treatment of other alkaline industrial solid wastes containing chromium (VI).

2. Experimental

2.1. Materials and set-up

This work is a part of our new process for manufacturing soda ash from sodium sulfate [17]. The sodium bicarbonate samples containing chromium (VI) came as the intermediate of carbonation of an aqueous sodium chromate solution.

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The chromium (VI) contents of samples were from hundreds to thousands parts per million. The sucrose and starch used were of reagent grade. The flour was purchased from a supermarket. Carbon dioxide was used as protection medium with a purity of 99.9%. The reduction was carried out in porcelain crucibles placed in a tube furnace with a temperature control unit.

2.2. Procedures

The samples were mixed with the reductants mentioned above in crucibles that were then put into the tube furnace. In order to ensure full and uniform contact of reductants with chromium, the reductants were prepared to an aqueous solution or slurry of given concentrations to keep a mass

ratio of solution to solid of 1/5 to 1/4. Carbon dioxide was first introduced into the tube furnace to displace the air in it, ensuring the reduction reaction to be carried out under an oxygen-free atmosphere. The furnace was heated to a predetermined temperature and maintained for a preset period. After that the tube was removed and cooled to the ambient temperature without stopping aeration of carbon dioxide. Then the samples were dissolved in water and the solutions were filtered with a 0.22 μm membrane filter. Chromium (VI) concentrations in the filtrates were measured using a spectrophotometer (Model 722S, Leng Guang Teck., Shanghai, China) at $\lambda = 372 \text{ nm}$, according to the method proposed by Oumedgbeur and Thomas [18]. The total chromium concentrations were determined with the method described in reference [19]. The reduced fraction (RNP) and the removed

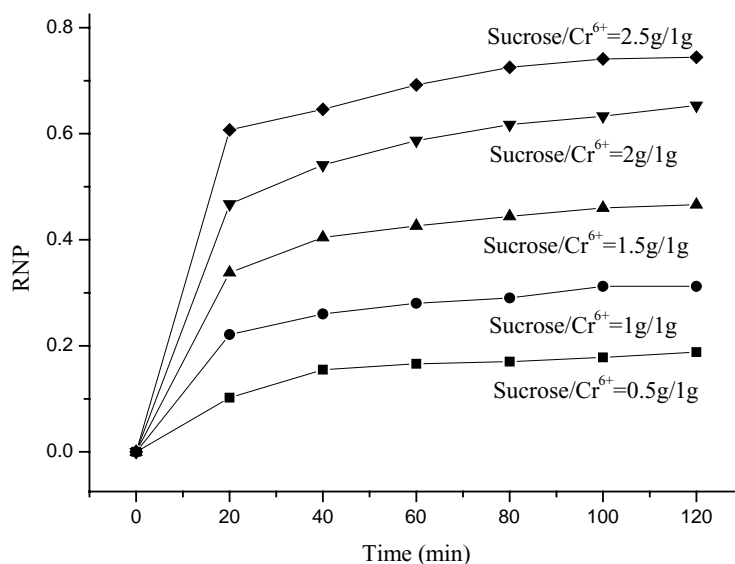


Fig. 1. RNP at different time and 200 °C (initial Cr⁶⁺ = 1.73%).

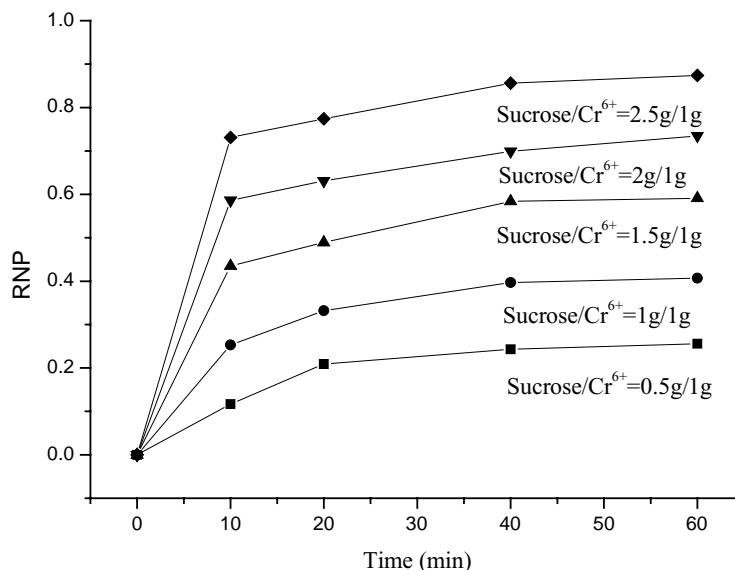


Fig. 2. RNP at different time and 300 °C (initial Cr⁶⁺ = 1.73%).

fraction (RLP) of chromium (VI) were calculated as follows:

$$RNP = \frac{\text{initial Cr}^{6+} - \text{Cr}^{6+} \text{ in filtrate}}{\text{initial Cr}^{6+}}$$

$$RLP = \frac{\text{initial Cr}^{6+} - \text{total Cr in filtrate}}{\text{initial Cr}^{6+}}$$

3. Results and discussion

3.1. Effect of temperature on reduction of chromium (VI)

The effect of temperature on the reduction reaction of chromium (VI) was examined at 200, 300, 400, 500, 600

and 800 °C, respectively. The results are shown in Table 1 and Figs. 1–5. It can be seen that higher temperatures favor both the reduction and removal of chromium (VI). At temperatures of or above 500 °C, the reduction can be expected to end in about 10–20 min. In order to remove chromium completely, however, the temperature should be above 600 °C. It is well known that chromium oxide hydrate (or chromium hydroxide) is amphoteric; it is almost insoluble at the pH range of 7–11, but much more soluble in strong acidic or basic solutions. When calcinated at a high temperature, chromium oxide hydrate becomes almost insoluble in both acidic and basic solutions. Table 1 indicates that 600 °C is a critical temperature for the removal of chromium. That seems to be consistent with the crystal formation temperature of chromium oxide. Yao [20] found

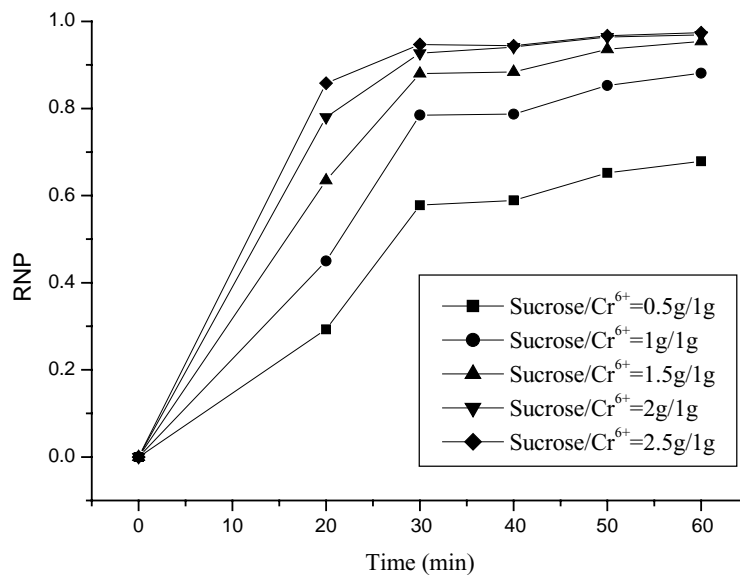


Fig. 3. RNP at different time and 400 °C (initial Cr⁶⁺ = 1.73%).

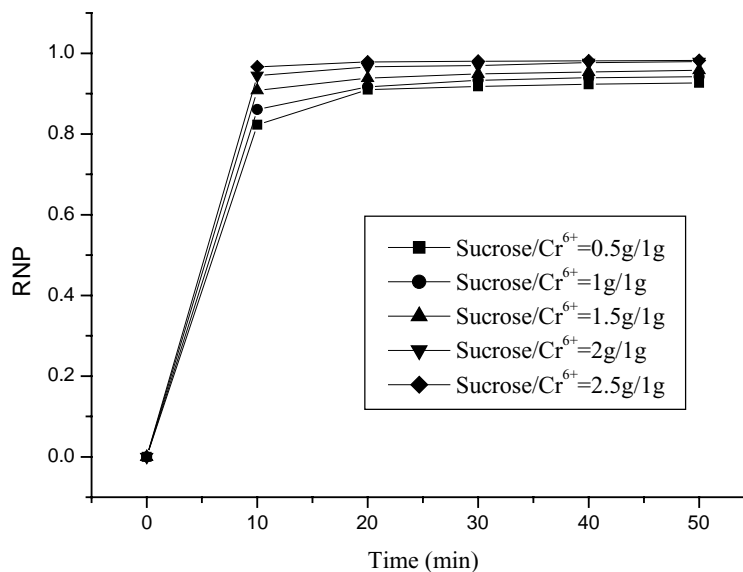


Fig. 4. RNP at different time and 500 °C (initial Cr⁶⁺ = 4.48%).

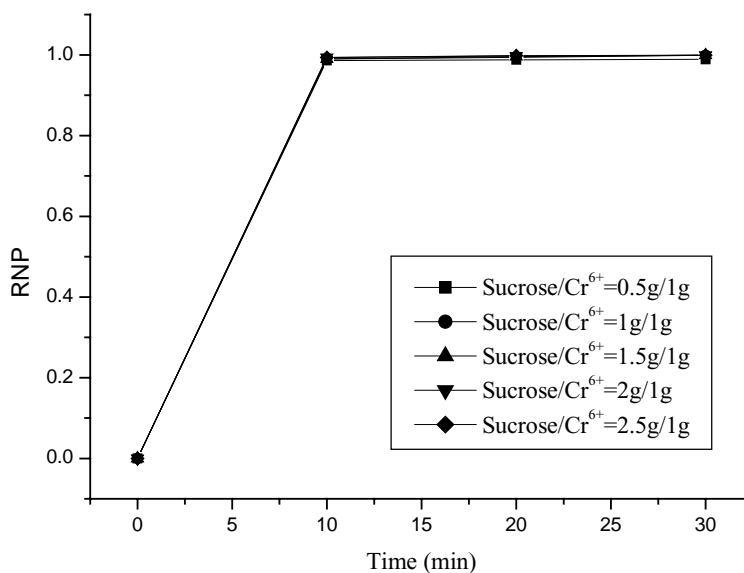


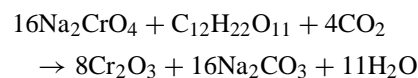
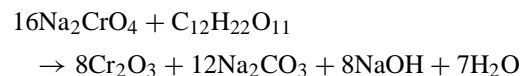
Fig. 5. RNP at different time and 600 °C (initial Cr⁶⁺ = 1.73%).

that chromium oxide is an amorphous powder below 400 °C and a hexahedral crystal above 580 °C. Chromium oxide hydrate starts to lose water at 130 °C and forms a crystal at about 400 °C. The insolubility of chromium (III) is attributed to the dehydration of chromium oxide hydrate and the crystallization of chromium oxide. Figs. 6 and 7 show the XRD (Model Rint 2400, Rigaku, Japan) patterns of the samples calcinated at 300 and 600 °C. In Fig. 7, besides those superposed with the peaks of Na₂CO₃, there are four peaks of Cr₂O₃ at 2θ angle = 36.56° (*d* = 2.46), 41.42° (*d* = 2.18), 58.46° (*d* = 1.58) and 65.34° (*d* = 1.43), while there is only one peak of Cr₂O₃ at 2θ angle = 41.30° (*d* = 2.18) in Fig. 6. This implies that the crystallization of chromium oxide possibly begins at 300 °C or even at 200 °C

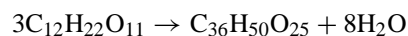
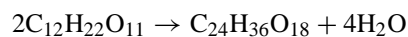
(the sample calcinated at 200 °C had the same XRD patterns as that calcinated at 300 °C), but the process finished at 580 °C.

3.2. Effect of amount of sucrose added on reduction of chromium (VI)

The effect of sucrose on the reduction of chromium (VI) was examined by adding different amounts of sucrose, i.e. 0.5, 1, 1.5, 2, 2.5 and 3 g with respect to 1 g Cr⁶⁺. Figs. 1–5 and Table 1 show the experimental results. The reduction rate and extent increased with increasing sucrose addition at all temperatures investigated. But the increases at or above 600 °C were neglectable. The reduction of chromium (VI) by sucrose can be represented by the following equations:



However, the reaction mechanism may vary with the increase of temperature and reaction time. It is known that sucrose pyrolysis starts at 160–180 °C [21–23]. At about 200 °C, sucrose is pyrolyzed as follows:



The reactions are catalyzed in alkaline media. Further pyrolysis takes place with the increase of temperature. Therefore, the reduction of chromium (VI) by sucrose might be a very complex process. In the early stage of reduction and

Table 1

Reduction fraction and removal fraction of chromium (VI) at different temperature and reactants ratios (initial Cr⁶⁺ = 100 mg/kg, time = 1 h)

| <i>T</i> (°C) | | Sucrose (g/g Cr ⁶⁺) | | | | | |
|---------------|-----|---------------------------------|-------|-------|-------|-------|-------|
| | | 0.5 | 1 | 1.5 | 2 | 2.5 | 3 |
| 200 | RNP | 0.435 | 0.538 | 0.676 | 0.733 | 0.784 | |
| | RLP | 0.430 | | 0.418 | 0.432 | 0.403 | |
| 300 | RNP | 0.664 | 0.749 | 0.803 | 0.808 | 0.833 | 0.836 |
| | RLP | 0.514 | 0.485 | 0.534 | 0.557 | 0.573 | 0.657 |
| 400 | RNP | 0.910 | 0.972 | 0.974 | 0.992 | | |
| | RLP | 0.905 | 0.892 | 0.882 | 0.95 | | |
| 500 | RNP | 0.973 | 0.985 | 0.987 | 0.988 | 0.989 | 0.991 |
| | RLP | 0.927 | 0.937 | 0.938 | 0.928 | 0.946 | 0.945 |
| 600 | RNP | 0.984 | 0.993 | 0.993 | 0.996 | | |
| | RLP | 0.972 | 0.992 | 0.987 | 0.991 | | |
| 800 | RNP | 0.996 | 0.996 | 0.996 | 0.996 | 0.996 | 0.996 |
| | RLP | 0.989 | 0.991 | 0.992 | 0.988 | 0.994 | 0.994 |

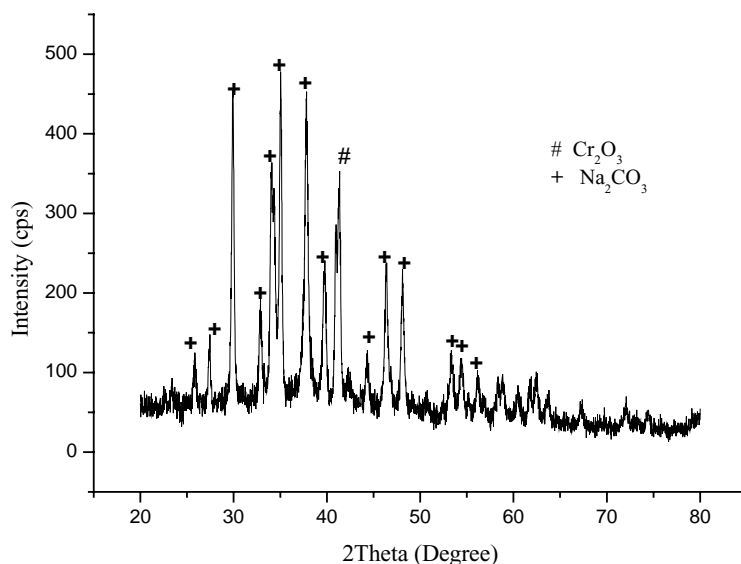


Fig. 6. XRD diagram of the sample calcinated at 300 °C.

at a relative low temperature, sucrose reacts with chromium (VI) and degrades simultaneously, and the reactions are homogeneous. In the late stage of reduction and at a relative high temperature, sucrose decomposes completely and it is carbon and the likes that react with chromium (VI), and the reactions are heterogeneous. Therefore, the reaction rate is faster and the effect of amount of sucrose on the reduction is more significant in the early stage of reduction.

3.3. Effect of reduction time on reduction of chromium (VI)

The effect of time on the reduction of chromium (VI) can also be seen from Figs. 1–5. It can be found that reduction time is strongly related with temperature. As pointed out

above, at or above 500 °C, the reduction can be expected to end in about 10–20 min. But it needs much more time below 400 °C. That means that the reduction reactions have high activation energies and temperature is the key factor affecting the reduction.

3.4. Effect of initial chromium (VI) content on reduction of chromium (VI)

Fig. 8 shows the reduced fraction and the removed fraction of chromium (VI) in samples with different initial chromium (VI) contents. It is indicated that the reduction is hardly related with initial chromium content at 600 °C. With the increase of chromium (VI) content from hundreds to thousands

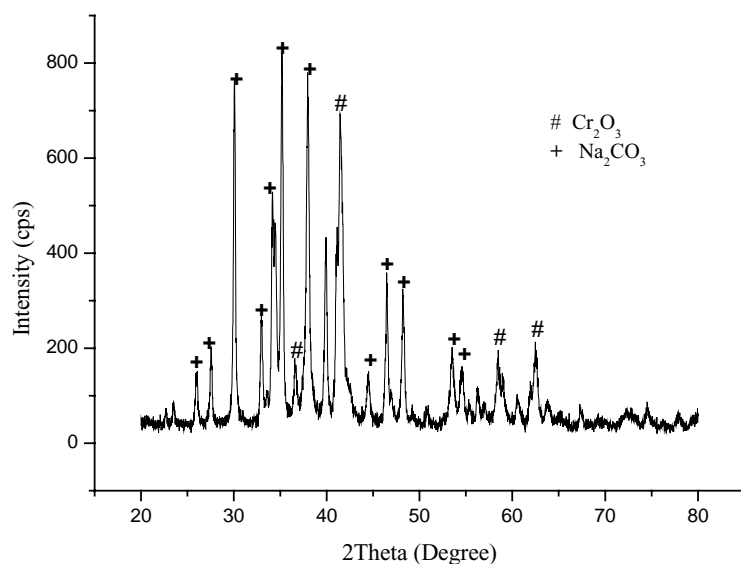


Fig. 7. XRD diagram of the sample calcinated at 600 °C.

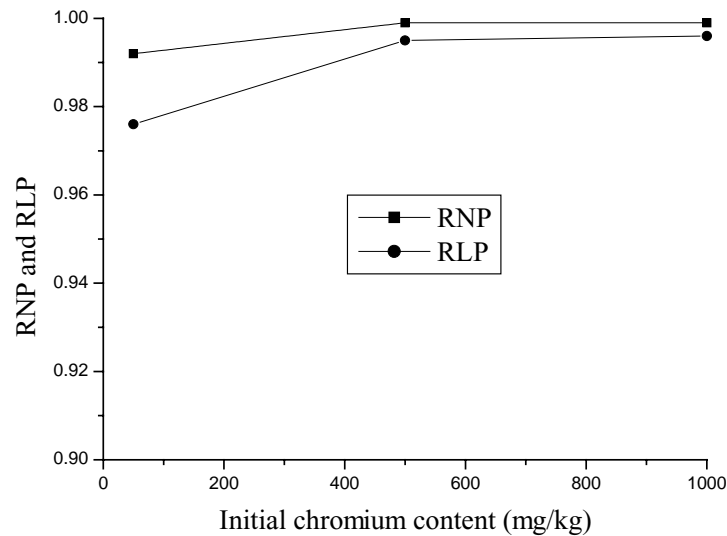


Fig. 8. RNP and RLP for different initial chromium content (sucrose/chromium = 1 g/1 g; reduction time = 1 h; temperature = 600 °C).

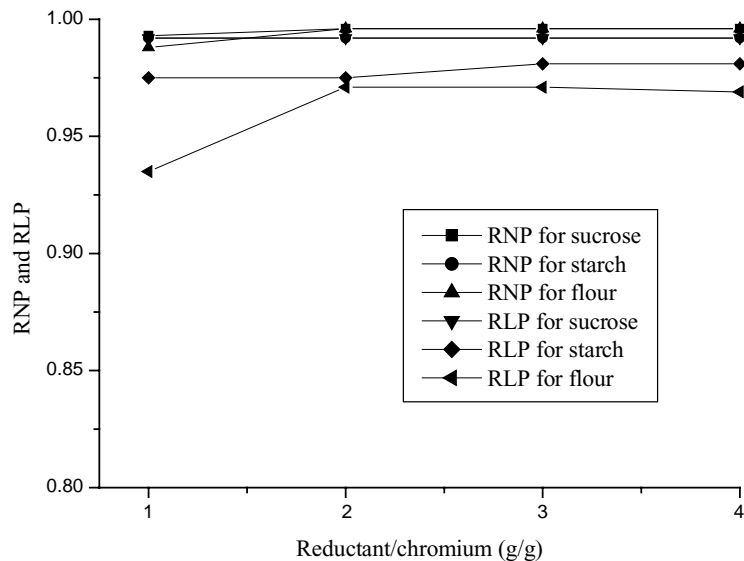


Fig. 9. RNP and RLP for different reductants (initial chromium content = 100 mg/kg; time = 1 h; temperature = 600 °C).

parts per million parts of a solid sample; chromium (VI) can almost be reduced completely. Nevertheless, a comparison of Figs. 1–4 and Table 1 suggests that at or below 500 °C, different initial chromium (VI) contents result in differences in reduced fractions, and the differences increase with the decrease of temperature and amount of sucrose.

3.5. Effect of reductants on reduction of chromium (VI)

Fig. 9 shows the reduced fraction and the removed fraction of chromium (VI) with sucrose, starch or flour as reductants. It can be found that starch and flour have almost the same reduction efficacy as sucrose. As far as the removed fraction is concerned, however, starch and flour exhibit slightly poorer reduction ability than sucrose. That is possibly because they have different molecular structures from sucrose,

and flour can only dissolve in water partly. It means that the reduction reaction takes place easily. Some cheaper materials may be used as reductants only if they could fully contact with chromium (VI).

4. Conclusions

Under oxygen-free conditions, chromium (VI) in alkaline solids can be reduced by sucrose, starch or flour through calcination. Temperature is a key factor affecting the reduction. At temperatures of or above 600 °C, the reduction can be expected to finish in about 10–20 min and chromium (III) can be transformed to an insoluble crystal of chromium oxide. The increase in amount of reductant benefits the reduction, but this effect is unobvious above 600 °C. All the three kinds

of reactants investigated, i.e., sucrose, starch and flour, can effectively reduce chromium (VI) of a level from hundreds to thousands parts per million.

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