Effect of Ion Water Washing of Neutralized Sludge Contaminated by High Concentrations of Chloride

Chiharu Tokoro1,*, Yuji Oda1, Shuji Owada1 and Hiroshi Hayashi2

1Department of Resources and Environmental Engineering, School of Creative Science and Engineering, Faculty of Science and Engineering, Waseda University, Tokyo 169-8555, Japan
2Central Research Institute, Mitsubishi Materials Corporation, Iwaki 971-8101, Japan

The effects of NO3− and SO42− ions on chloride ion removal from neutralized sludge were investigated to determine if removal of chloride ions enabled the use of sludge for cement production. An artificial sludge prepared from iron, calcium and chloride that primarily consisted of two-line ferrihydrite was prepared. Chloride ions in the sludge were easily washed out by distilled water, NO3− water or SO42− water to levels below those specified in the standard for Eco-cement production (1,000 mg/kg), but the washed sludges did not meet the standard for ordinary Portland cement (350 mg/kg). Conversely, artificial sludge prepared from aluminum, calcium and chloride mainly consisted of low crystalline boehmite with other minor components. Chloride ions in this sludge were only reduced to below those specified in the standard for the ordinary cement production if SO42− water was used to wash the sludge. The filtration rate during washing using SO42− water was faster than when distilled water or NO3− water was used because SO42− ions were adsorbed onto the sludge particles and the absolute value of the zeta potential of the sludge particles decreased. Overall, sludge washing using SO42− water was the best process for chloride ion removal and efficient filtration.


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1. Introduction

Minimizing resource consumption and waste generation is a frequent topic of discussion worldwide that is especially important in Japan because of a shortage of landfill sites for disposal as well as a stable supply of resources. In 2010, a total of 389.746 million tons of industrial waste was discharged, while the total discharge of sludge was 173.629 million tons, which accounted for 44.5% of the industrial waste.1) Accordingly, more efficient recycling and a reduction of the quantity of sludge generated are necessary in Japan.

Several waste and by-products are utilized by the cement industry as raw materials or thermal sources for cement production.2−5) However, sludge contaminated with high quantities of chloride cannot be utilized for cement production because the chloride ions decrease the quality of cement and make the operation unstable. As a result, the concentration of chloride in cement is limited to 350 mg/kg in ordinary Portland cement6) and 1,000 mg/kg in Eco-cement (cement in which municipal waste combustion ash and sewage sludge are utilized as the main raw materials).7)

Neutralized sludge from industrial wastewater sometimes contains high quantities of chloride and requires efficient washing of chloride for utilization in cement production.8−11) Many researchers have reported that when metal hydroxides are the main component of the sludge chloride ions cannot be removed from the sludge by washing with water alone due to the chemical affinity between chloride ions and sludge components.9−11) However, the mechanism for uptake of chloride ions by sludge components and their removal during sludge washing have not been described in detail to date.

This study was conducted to investigate chloride ion removal from neutralized sludge using several types of ionic water. Specifically, the mechanism of chloride ion removal during the washing process was evaluated to determine if the use of ionic water for the removal of chloride ions from sludge to be used in cement production was feasible. To study the uptake/removal mechanism of chloride ions in sludge in detail, we used two types of artificial sludge that were neutralized using calcium hydroxide, one prepared from ferric and chloride ions solution (Fe–Ca–Cl sludge) and another prepared from aluminum and chloride ions solution (Al–Ca–Cl sludge). These ferric and aluminum ions are the main components in actual neutralized sludge and calcium hydroxide is also the most commonly used neutralizer owing to its good performance and effective solid/liquid separation.

This study was conducted to compare the removal of chloride ions from Fe–Ca–Cl sludge or Al–Ca–Cl sludge washed with distilled water, nitric acid (NO3−) water and sulfuric acid (SO42−) water, and to discuss the mechanism by which the uptake/removal of chloride ions occurred. To accomplish this, we repeated batch washing experiments five times and then quantitatively analyzed the concentration of chloride ions in washing water and sludge. We also evaluated the sludge before/after washing by X-ray diffraction (XRD) and Fourier transformed infrared spectrometry (FT-IR).

In general, several researches have proposed that adsorption affinity to hydroxides is SO42− >> NO3− > Cl− in high concentration of acid solution.13) Additionally, high concentration of SO42− sometimes promotes dissolution of sludge containing Cl− because it products new precipitation with metallic ions in the sludge. Therefore, SO42− or NO3− water has potential to remove Cl− from the sludge consisting of hydroxides. After washing using these ion water, effluent is consisted of several acid and dissolved components from the sludge and additional neutralization is needed. However, it is expected that the amount of new precipitated sludge from effluent treatment is small.

During washing of sludge, good solid/liquid separation is required in addition to efficient chloride removal. Therefore,
we also compared the filtration rate during the washing process and evaluated differences among sludges based on the zeta potential of the sludge before/after washing.

2. Experimental Procedure

2.1 Standard and reagents

All chemicals and solutions used in this study were of analytical grade and were purchased from Wako Pure Chemicals, Inc., Japan. The ferric, aluminum and chloride solutions were prepared from FeCl₃·6H₂O, AlCl₃·6H₂O and 12N HCl, respectively. Ca(OH)₂ was used as neutralizer. The NO₃⁻ washing water and SO₄²⁻ washing water were prepared from NaNO₃ and Na₂SO₄, respectively. All experiments were conducted at 25°C. In addition, all experiments were performed at least in triplicate and the error was confirmed to be within 1%.

2.2 Preparation of artificial sludge

Artificial Fe–Ca–Cl sludge and Al–Ca–Cl sludge were prepared as follows. Briefly, 0.6 dm³ of 0.1 M Fe(III) or 0.1 M Al(III) and 1 M Cl(–I) were initially prepared in 1 dm³ beakers and neutralized by the addition of about 0.1 dm³ of 20 mass% Ca(OH)₂ slurry to give a pH of 7. After agitation at 5000 rpm for 30 min using a magnetic stirrer, the suspension was filtered through a 0.45 µm membrane filter (Advantec, Japan).

2.3 Washing experiments

Freshly prepared artificial sludge was prepared for all washing experiments conducted in this study. Three types of washing water, deionized (DI) water, water containing 2000 mg/L of washing water, and water containing 2000 mg/L of washing water and SO₄²⁻ washing water were used.

A total of 80 cm³ of artificial sludge suspension was filtered through a 0.45 µm membrane filter and the residue was then re-dispersed in 40 cm³ of washing water in a 100 cm³ conical beaker and stirred at 1000 rpm using a magnetic stirrer. The suspension was then passed through a 0.45 µm membrane filter again. The re-dispersion in washing water and filtration were repeated five times, after which the concentration of Cl⁻, NO₃⁻ or SO₄²⁻ in filtrate were analyzed by ion chromatography (IC-2001, Tosoh, Japan) and the concentration of chloride ions in the residue were analyzed by the Volhard method. The concentration of iron, aluminum, calcium and sodium in the residue was analyzed by X-ray fluorescence (XRF) (PW1480/1404, PANalytical, Japan).

2.4 XRD analysis

The chemical forms of the sludge were evaluated by XRD analysis (Geiger flex RAD-IR, Rigaku, Japan). XRD patterns of the sludge before/after washing were obtained using a copper target (Cu Kα), a crystal graphite monochromator, and a scintillation detector. The equipment was operated at 40 kV and 30 mA by step-scanning from 2° to 80° 2θ at increments of 0.02° 2θ and a scan speed of 2°/min. A crystal sample holder was used and the diffractograms were not corrected by background disfraction. The filter residue was freeze-dried at −45°C for 24 h prior to analysis.

Two-line ferrihydrite and low crystalline boehmite were synthesized as reference materials. Two-line ferrihydrite was synthesized from 10 mg/dm³ Fe(III) solution prepared using Fe(NO₃)₃·9H₂O at pH 5 and an ionic strength of 0.05 using 1M HNO₃ and 1M KOH to regulate the pH and ionic strength, respectively. Low crystalline boehmite was synthesized from 20 mg/dm³ of Al(III) solution prepared using Al(NO₃)₃·9H₂O at pH 9 and an ionic strength of 0.05 using 1M HNO₃ and 1M KOH to regulate the pH and ionic strength, respectively.

2.5 FT-IR analysis

The sludge was also analyzed during the washing experiments after freeze-drying using FT-IR spectroscopy (FT-IR 4200, JASCO, Japan). Pellets for FT-IR were prepared by compression molding with KBr. The mixing ratio of the sample to KBr was fixed at 0.3 mass% and FT-IR spectra were obtained using transmission FT-IR spectroscopy.

2.6 Zeta potential measurement

Measurement of the zeta potential was conducted using an electrophoresis light scattering spectrophotometer (ELS-8000, Otsuka Electronics, Japan). To accomplish this, suspensions of the sludge prepared during the washing experiments prior to filtration were dispersed in an ultrasonic bath for 5 min and then rapidly analyzed by spectrophotometry.

2.7 Measurement of filtration rate

The quantity of filtrate and time of filtration were measured during suction filtration of a suspension of the sludge under 0.005 MPa. For filtration, a filter holder with a 250 dm³ funnel (Sartorius, Germany) and 0.45 µm membrane filter were used. The filtration rate was determined as follows:

\[ V = \frac{Q}{S}, \]

where \( Q \) (m³/h) is the flow rate and \( S \) (m²) is the filtration area. In this study, the effective area of the filtration equipment was 1.25×10⁻³ m².

3. Results and Discussion

3.1 Effect of ionic water on removal of chloride from the sludge

The concentrations of chloride ions in the artificial Fe–Ca–Cl sludge and Al–Ca–Cl sludge before/after washing using distilled water, NO₃⁻ water and SO₄²⁻ water are shown in Figs. 1 and 2. The concentrations of iron and calcium in the sludge are shown in Table 1. For the artificial Fe–Ca–Cl sludge, there was little difference in chloride removal by distilled water, NO₃⁻ water and SO₄²⁻ water, and most of the chloride ions were removed from the sludge during the first washing process. Salingar et al. also proposed that 92% of the chloride ions in a sludge in which Fe(III) was the main component could be removed by a single wash using water. As shown in Table 1, the residual concentration of chloride in the sludge after five washes was less than 900 mg/kg, which did not meet the standard for ordinary Portland cement (350 mg/kg), but did meet the standard for Eco-cement (1,000 mg/kg).
For Al-Ca-Cl sludge, there was a large difference in chloride removal between distilled water, NO$_3^-$ water and SO$_4^{2-}$ water. A large amount of chloride (33,000 mg/kg) remained in the sludge when distilled water was used, while removal of additional chloride from the sludge was achieved when ionic water was used. Following washing with NO$_3^-$ water, the residual concentration of chloride was 4,400 mg/kg, which exceeded the standard for cement production. In contrast, when SO$_4^{2-}$ water was used, the residual concentration of chloride was less than 300 mg/kg, which met the standards for both ordinary Portland cement and Eco-cement.

NO$_3^-$ or SO$_4^{2-}$ concentration taken in sludge during five times washing was shown in Fig. 3. Both for Fe-Ca-Cl and Al-Ca-Cl sludge, more SO$_4^{2-}$ ion was uptake than NO$_3^-$ ion. Especially for Al-Ca-Cl sludge, in the first washing by SO$_4^{2-}$ ion water, a lot of SO$_4^{2-}$ was uptake to the sludge. This result suggests that new precipitates could be formed between Al-Ca-Cl sludge and SO$_4^{2-}$ ion water during the first washing. In any case, these residual SO$_4^{2-}$ or NO$_3^-$ concentration in the sludge after washing have no problem for cement utilization.

In addition, pH was decreased until around 6.5 at the first washing, while it was increased gradually during following washing up to 7.5.

### 3.2 Mineralogical changes in sludge following washing

Figure 4 shows a comparison of the XRD patterns of artificial Fe-Ca-Cl sludge before/after washing five times using distilled water, NO$_3^-$ water and SO$_4^{2-}$ water. All XRD patterns showed two broad bands at 34° 2θ and 61° 2θ, which were the same positions as observed for two-line ferrihydrite.$^{14}$ These results suggest that artificial Fe-Ca-Cl sludge mainly consisted of two-line ferrihydrite, and that the mineral form was not changed by washing with ionic water. Chloride ions generally form outer-sphere complexes with hydro ferric oxide, and not many chloride ions can be taken up by ferrihydrite.$^{12,15}$ However, as shown in Table 1, residual chloride ions that exceeded the standard for ordinary Portland cement production were left behind in Fe-Ca-Cl sludge after washing with any type of water. These findings suggest that some amorphous component other than two-line ferrihydrite strongly bound the chloride ions into the sludge. As shown in Table 1, the artificial Fe-Ca-Cl sludge contained 0.28% calcium, and that the amount of calcium did not change after washing. In this study, calcium ferrite (CaFe$_2$O$_4$) was thermodynamically saturated in an artificial Fe-Ca-Cl formation$^{16}$ as shown in Table 2. Moreover, there was the potential for formation of Ca–Fe hydroxalites, which could take up chloride ions in the Fe-Ca-Cl sludge.
Figure 5 shows a comparison of the XRD patterns of artificial Al–Ca–Cl sludge before/after washing five times with distilled water, NO$_3^-$ water and SO$_4^{2-}$ water. This figure also shows the XRD patterns of low crystalline boehmite, which has broad bands at 29° 2θ, 39° 2θ and 48° 2θ. Although the artificial Al–Ca–Cl sludge had broader and weaker peaks at the same positions before washing as observed for low crystalline boehmite, these peaks became sharper and clearer after five washes with distilled water or NO$_3^-$ water. These results suggest that a portion of the sludge dissolved and minor new components formed in the sludge after washing with SO$_4^{2-}$ water. In this study, gypsum (CaSO$_4$·2H$_2$O) and aluminum sulfate were thermodynamically saturated during SO$_4^{2-}$ water washing as shown in Table 3. Additionally, ettringite (Ca$_6$Al$_2$(SO$_4$)$_3$(OH)$_{12}$·26H$_2$O) is also known to be a stable component in Al–Ca–SO$_4$ aqueous systems. Although ettringite was thermodynamically unsaturated in this study, there was the potential for adsorption of Ca or SO$_4$ ions to boehmite because of high chemical affinity between Al, Ca and SO$_4$. To evaluate mineralogical changes in the Al–Ca–Cl sludge after washing, we also analyzed the FT-IR spectrum (Fig. 6). The band at approximately 600 cm$^{-1}$ could be assigned to a mixed contribution of Al–O stretching and bending for AlO$_6$, which has one particularly long Al–O bond with respect to the other five bonds. Prior to washing, this band shifted toward a low wavenumber, which suggests that the structure of low crystalline boehmite was ambiguous in the sludge before washing. The band at 950 cm$^{-1}$ corresponds to the...
stretching mode of Al–O which is observed in both aluminum hydroxide and low crystalline boehmite. This band could be clearly distinguished in the sludge before and after washing with SO$_4^{2-}$ water, while it shifted or became smaller after washing using distilled water or NO$_3^-$ water. The small band at approximately 1050 cm$^{-1}$ corresponds to the stretching mode of Al–O, which is only observed in low crystalline boehmite. This band was unclear in the sludge before washing or after SO$_4^{2-}$ water washing, while it was clear in the sludge after washing using distilled water or NO$_3^-$ water. The band at approximately 1060 cm$^{-1}$ and 1400 cm$^{-1}$ corresponds to the bond angle bending mode of S–O and the stretching mode of N–O, respectively. These bands suggest that adsorption of NO$_3^-$ or SO$_4^{2-}$ occurred during washing with NO$_3^-$ water or SO$_4^{2-}$ water.

All of the FT-IR spectra suggest that components of the Al–Ca–Cl sludge before washing or after washing with SO$_4^{2-}$ consisted of combinations of aluminum hydroxide and low crystalline boehmite, which had a structure that became clearer after washing with distilled water or NO$_3^-$ water. Overall, the results of FT-IR analysis coincide with those of XRD analysis.

3.3 Effect of washing with ionic water on filtration rate

The filtration rate of the Fe–Ca–Cl sludge and Al–Ca–Cl sludge during five washes with distilled water, NO$_3^-$ water and SO$_4^{2-}$ water are shown in Figs. 7 and 8. In the cases of Fe–Ca–Cl sludge and Al–Ca–Cl sludge, the filtration rate was largest during SO$_4^{2-}$ water washing, followed by NO$_3^-$ water washing and distilled water washing.

The filtration rate generally depends on the crystallinity or particle size of the components in the sludge and the surface electric potential at the solid/liquid interface between the sludge and the washing water. As shown in Figs. 9 and 10, the zeta potential of the sludge decreased considerably after washing with SO$_4^{2-}$ water, which suggests that many SO$_4^{2-}$ ions were adsorbed onto the surface of the sludge particles. In the case of NO$_3^-$ water washing, the zeta potential of the sludge also decreased because of the adsorption of NO$_3^-$ ions onto the sludge; however, this decrease was not as great as that observed during washing with SO$_4^{2-}$ water. Conversely, the zeta potential showed increases or decreases during washing with distilled water owing to the desorption of chloride, calcium and aluminum ions from the sludge.

The relationship between the zeta potential and the filtration rate was found to be negatively correlated (Fig. 11), which suggests that when the absolute value of the zeta potential was small, particles of sludge were agglomerated together and the pathway of the washing water could form inside the sludge.
4. Conclusion

The effects of NO₃⁻ or SO₄²⁻ on removal of chloride ions from sludge during washing were investigated. Artificial sludge prepared from iron, calcium and chloride mainly consisted of two-line ferrihydrite and chloride ions at levels exceeding the standards for cement utilization. However, when SO₄²⁻ water was used for washing, the chloride levels were reduced to below the standard for ordinary cement production.

The effects of NO₃⁻ or SO₄²⁻ ions on the filtration rate during washing of sludge were also investigated. During washing using SO₄²⁻ water, the filtration rate was faster than that of distilled water or NO₃⁻ water because SO₄²⁻ ions were adsorbed onto the sludge particles and the absolute value of the zeta potential of the sludge particles decreased. Overall, sludge washing using SO₄²⁻ water produced the best results for chloride ion removal and filtration.

REFERENCES