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<td>引用</td>
<td>長崎大学大学院工学研究科研究報告, 48(90), pp.45-56; 2018</td>
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Chemistry of Fluoride Leaching and Associating Influential Factors in Plaster Board Waste

by

Venkataraman SIVASANKAR* and Kiyoshi OMINE**

Plaster board waste generated from industries, usually contains major proportion of calcium as calcium sulfate. In addition, fluoride is remarkably one among the constituents of this waste material. Experimental studies were conducted to determine the fluoride leaching as a function of particle size, pH of leaching solvent (distilled water) and water: PBP ratio. The influence of sodium salts on the leaching of fluoride from PBP was studied. It was explored that one gram of plaster board waste contains 18.54 mg F per gram of PBP. High leaching of 3.70 mg F per liter was studied at pH 6.02 with Ca\(^{2+}\) and TDS contents of 1050 mg L\(^{-1}\) and 1640 mg L\(^{-1}\) respectively. The influence of fluoride leaching by sodium phosphate recorded a high value of 12.75 mg L\(^{-1}\) with no detectable amount of calcium ions. The leaching mechanism was predicted significantly by the exchange of Na\(^{+}\) and Ca\(^{2+}\) ions. The leaching rate as a consequence of shaking and stirring dynamics was also investigated at different conditions.

**Key words:** Plaster board; fluoride leaching, characterizations

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1. Introduction

Every year, the discharge of waste plaster board (PB) is estimated to be 1.091 million tons in Japan. The PB discharge includes 0.796 million tons from demolition works and 0.295 million tons from new construction works. The estimated discharge is expected to reach 2.5 million tons in 30 years. The hazardous elements present reported in PB are arsenic (As), cadmium (Cd) and fluoride (F). Fluoride is considered as one of the major pollutants in Japan [1]. The Japanese Environmental Standard limit for fluoride is 0.8 mg L$^{-1}$ [2]. Fluoride contamination in drinking water and its associated problems are well known [3]. It is reported [4] that groundwater fluoride causes disease in an exponential manner among the people ($10^8$) across the world. A recent study disseminated that children victims of dental fluorosis become insufficiently nutritious [5] and the high concentration of fluoride could cause learning disabilities in children [6]. Excessive fluoride ingestion occurs through foodstuff [7], toothpaste and products of dental health [8] in addition to drinking water. Fluoride enrichment in groundwater at the Western Part of Kumamoto area in Japan was studied [9] and reported that shallow groundwater and deep groundwater samples of 58% and 26% were found above the safe fluoride level of Japanese standard. The hydro-chemical reactions of Toki granite containing fluorite and mica enriched the fluoride level in groundwater in the Mizunami area of central Japan [10]. Yamada and co-workers [11] studied the leaching and control of fluoride in plasterboard powder using light burned magnesite. Sakanakura et al. [12] explored the control of soil property over fluoride leaching from plaster board. In the present research contribution, the fluoride leaching from PB powder as a consequence of its interaction with other associating ions which are commonly present in the soil environment has been studied. This study has been envisaged to cater for better insight in choosing the suitable soil environment where the leaching can be controlled by immobilizing fluoride from PB waste.
2. Materials and methodology

2.1 Instrumental characterizations

PB powder was characterized using FTIR (Nexus 870 FTIR, Thermo Scientific), X – Ray Diffraction (Rigaku, MiniFlex 600 Benchtop XRD, operated using 0.625 DS and 10 mm HIS with SS of 13.0 mm at 40 kV and 15 mA), FE – SEM (JEOL JSM – 7500FA) with EDS system and DTG (DTG – 50, Shimadzu simultaneous DTA – TG Analyzer) studies. Fluoride was analyzed with Thermo Scientific Orion Versa Star using Orion fluoride ion – selective electrode (254792-001).

2.2 Fluoride leaching experiments

The waste plaster board (Fig. 1) was procured from an industry located at Omura, Japan. The PB sheets were initially processed by separating the wrappers on the surface followed by grinding into powder using steel mixer grinder. Then the powdered mass was oven – dried at 110˚C for 10 h and sieved for the particle size of 250 – 106 µm. The sieved PB powder was preserved in desiccator (to keep away the moisture) for experimental studies. Leaching experiments were carried out using a defined amount of PB powder in a volume of 0.1 L of distilled water. The shaking experiments
were run using Thomas (T - 2S) thermostatic shaking bath using amber-colored and glass – lid conical flasks of 0.2 L capacity. pH adjustments in solutions were done by 0.1 N HCl or NaOH solutions using pH meter. All the chemicals and reagents used in the study are of analar grade.

3. Results and discussion

3.1 Characterization of Plaster Board Powder (PBP)

The FE-SEM image shows the appearance of smooth, transparent and needle-like morphology of PBP at magnification of 10k. The colored images each for Ca, S and O elements are also represented in Fig. 2. The x – ray diffraction pattern (Fig. 3) reveals the presence of β – CaSO₄ . 0.5 H₂O and its anhydrite (syn) based on the DB card numbers 00-045-0848 and 00-037-1496 respectively. The crystallite size recorded for β form of CaSO₄ . ½ H₂O of 40 nm was less than that of its anhydrite form of 43 nm. The identification of α – SiO₂ (Card No. 01-089-8937) along with CaSO₄ (Card No. 01-070-0909) after heating the PBP at 1000˚C was evident from the thermal study. The amount of carbon was analyzed to be 0.633% by mass and the amount of material loss due to ignition was 8.74% by mass [13]. Although similar lattice angles were exhibited (α = β = 90˚), the angle (γ) in the heated PBP was 120˚ unlike in β – CaSO₄ . 0.5 H₂O with 90˚. The presence of bassanite form (CaSO₄ . ½ H₂O) in PBP could be characterized in the special region 3500 cm⁻¹ and 1600 cm⁻¹. In the mid – IR spectra (Fig. 4), the peaks at 3560 cm⁻¹ and 3600 cm⁻¹ are ascribed respectively to the symmetric (υ₁) and anti-symmetric (υ₃) stretch vibrational modes of water. The O–H bending vibration mode was observed at 1620 cm⁻¹. A sharp peak at 1140 cm⁻¹ with a shoulder at 1080 cm⁻¹ indicated the asymmetric stretching mode (υ₃) of SO₄²⁻ group. The combination modes of SO₄²⁻ and H₂O vibrations was reported to occur in the range 3130 – 3428 cm⁻¹ in bassanite in agreement with our study [14].
Fig. 2 FE – SEM images of plaster board powder (PBP)
3.2 Effect of contact time

The concentration of fluoride leaching as a function of time was carried out at 25°C using the PBP (particle size < 250µm) amount of 1 g (in 0.1 L of water as the leaching solvent) and shaking time was optimized for 4h. The amount of fluoride leached was 3.70 mg L\(^{-1}\) and calcium
along with fluoride was also analyzed to be 1000 mgL⁻¹ with the corresponding TDS value of 1940 mgL⁻¹. The aliquots which were drawn two times every hour were with an averaged pH of 6.85.

Fig. 5 Influence of pH on fluoride and calcium leaching in PBP (A) and plot of initial versus final pH; Conditions: agitation time – 4 h; Volume of LS – 0.1 L; Quantity of PBP – 1 g; Size of PBP < 106 µm

### 3.3 Effect of pH on fluoride leaching from PBP

The pH of a solution plays a significant role towards the leaching of fluoride in PBP. The effect of pH on the leaching of fluoride (Eq. 1) from PBP was studied from pH 3.04 to 10.92 as shown in Fig. 5A. The presence of CaF₂ in PBP leached less effectively under pH < 6 and pH > 10 in addition to the neutral pH. Under acidic conditions, the tendency towards the protonation of ionisable fluoride from CaF₂ increased on decreasing the pH and resulting in the formation of hydrofluoric acid, a very weak acid. As a consequence of HF formation, the fluoride leaching decreased on decreasing the pH (Eq. 2). Conversely under basic conditions, the generation of hydroxide ions (between pH 8 and 10) tend to combine with Ca²⁺ ions and pulls the equilibrium towards the right hand side (Eqs. 1 and 3) by releasing more F⁻ ions. As the OH⁻ ion was consumed, the solution was controlled with its final pH of 7. Nevertheless, at pH > 10, the lessening of fluoride leaching might be attributed to the exchange of F⁻ and OH⁻ in Ca(OH)₂ to form Ca (OH)F and CaF₂ (Eq. 4 and Eq. 5). The exchange mechanism resulted in the ejection of OH⁻ in solution and there by increased the pH as shown in Fig. 5B.

\[
PBP \rightarrow CaF_2 \rightleftharpoons Ca^{2+} + 2F^- \quad \text{(1)}
\]

\[
2F^- + 2H^+ \rightarrow 2HF \quad \text{(under acidic conditions)} \quad \text{(2)}
\]
The leaching curves for calcium and fluoride are directly proportional to each other. The similarity in gradation patterns could be pertinent to the association of calcium and fluoride ions reversibly to form CaF$_2$ or the dissociation of CaF$_2$ into the constituent ions at the respective conditions. The fluoride leaching from PBP was studied based on the effect of the quantity of PBP with different H$_2$O/PBP ratios (Fig. 6A). It is apparent from the fluoride leaching graph that the ionisable fluoride was studied proportional to the amount of PBP. The amount of fluoride leached from 3.12 mgL$^{-1}$ to 6.25 mg L$^{-1}$ for the respective PBP: H$_2$O ratios from 1:200 to 1:10. Despite two times increase in fluoride leaching, the leached amount of Ca$^{2+}$ was 1020±60 mgL$^{-1}$ in the studied range of PBP: water ratio. It can also be taken into account that, the more the quantity of PBP, the more the amount of CaF$_2$ in it and ultimately resulting in the leaching of more fluoride in water. But the amount of leachable calcium ions become saturated with the volume of leaching solvent (LS), water. The final pH of the resulting solutions was recorded in the range of 6.84 – 7.10.

\[
Ca^{2+} + 2OH^- \rightarrow Ca(OH)_2 \text{(under basic conditions)} \quad \ldots \ldots (3)
\]
\[
Ca(OH)_2 + F^- \rightarrow Ca(OH)F + OH^- \quad \ldots \ldots (4)
\]
\[
Ca(OH)_2 + 2F^- \rightarrow CaF_2 + 2OH^- \quad \ldots \ldots (5)
\]

**Fig. 6** Influence of PBP: Water ratio on fluoride leaching (A) Ionic effect on fluoride leaching by shaking and stirring agitations; **Conditions:** pH – 6.05$^*$; quantity of PBP – 1 g; Sodium salt – 5 g;
(PBP: Sodium salt ratio – 1:5); agitation time – 4h (shaking) & 3h (stirring); volume of LS – 0.1 L; size of PBP < 106 µm

3.4 Effect of other associating anions

The influence of anions such as chloride, nitrate, acetate, hydrogen carbonate, carbonate, sulfate, tetra-borate and phosphate on the leaching of fluoride from PBP was performed as shown in Fig. 6B. This study was carried out with a notion of imitating the practical soil environments with varied proportions of minerals which are naturally present. In order to fulfill this, the PBP was added with five proportions of sodium compounds by maintaining the PBP: NaAn ratio from 1:1 to 1:5. The conditions were envisaged with a purpose of catering the real systems where the soil and groundwater contaminated with fluoride under the influence of plaster powder. The following chemistry (Eq. 6) played a significant role towards the solubility of NaF and thereby influencing contamination in the environment [15].

\[ CaF_2 + NaA_n \rightleftharpoons NaF + CaA \ (or) CaA_n \ (or) Ca_3A_n \]  

\[ \text{where } A \text{ is a monovalent or bivalent or trivalent anion } & n = 1, 2 \text{ and } 3 \]

Based on the results, the leaching of fluoride was observed with a varied in the range of 0.1 – 1.13 mgL⁻¹ between shaking and stirring methods. On comparing the two agitation methods, the positive gradation in fluoride increase was quite explicable except the two systems in which PBP was added to phosphate and groundwater. The effectiveness of stirring dynamics than shaking was discussed in the case of fluoride sorption systems [16]. Among the influencing anions, the maximum leaching of fluoride was highly driven by phosphate followed others as hydrogen carbonate > carbonate = sulfate > acetate > nitrate > chloride > tetra-borate. The contemporary ion, Ca²⁺ was decreased when the influential ions were sulfate and tetra-borate. This may be due to the backward reaction which associates the calcium and its counter ions or the enhanced precipitation of calcium borate which lessens the Ca²⁺ concentration. On accompanying the other sodium compounds such as chloride, nitrate and acetate, the Ca²⁺ concentration was higher (1.8 – 3 times) than its usual solubility in water. This corroborates the enhanced leaching of Ca²⁺ in the presence of sodium compounds which tend to drive the forward reaction. In cases like sodium carbonate, sodium hydrogen carbonate and sodium phosphate, the presence of Ca²⁺ in solution was undetectable due to the complete precipitation of calcium carbonate and phosphate. It is quite
evident that calcium and fluoride in groundwater are inversely proportional to each other [17]. In supporting the above statement, the concentration of fluoride surmounted when Ca$^{2+}$ in solution becomes unaddressed.

In addition, the impact of groundwater on fluoride leaching was studied by shaking (and stirring) 1 g of PBP in 0.1 L of groundwater. The leached content of fluoride in groundwater was 4.02 mg L$^{-1}$ and 3.60 mg L$^{-1}$ by shaking and stirring agitations respectively with the respective 4 h and 3 h of optimized agitation time. The groundwater (initial TDS = 83 mg L$^{-1}$) with neutral nature (pH 7.08) raised to the highly alkaline nature with pH of 8.82 (shaking) and 7.73 (stirring) with respective Ca$^{2+}$ concentration of 1200 mg L$^{-1}$ and 940 mg L$^{-1}$. The final pH of leached solutions were neutral (pH 7.35±0.15) after agitation with chloride, sulfate and nitrate salts and the exception was the one used with acetate, in which the solution was buffered with pH 6. For the other solutions agitated with borate, carbonate, hydrogen carbonate and phosphate, the final pH was measured to be 9.1, 11.4, 7.9 and 12.0 respectively. Nevertheless, the pH difference was meagre (±0.4) in these systems.

![Fig. 7 Profile of continuous attempts on the leaching of fluoride using 1 g PBP (A) Profiles on the leaching of calcium and total dissolved solids from PBP (B) Conditions: agitation time – 4 h; Volume of LS – 0.1 L; Quantity of PBP – 1 g; Size of PBP < 106 µm](image)

In order to quantify the total amount of fluoride present in 1 g of PBP, a series of agitations was attempted. During every attempt, the undissolved PBP was again taken with a fresh volume (0.1 L) of distilled water and agitated for its optimized time at pH 6.05. A total of seven attempts
was taken to dissolve 1 g of PBP as shown in Fig. 7A. The graph illustrates the gradual decrease in the concentration of fluoride from 3.7 mg L⁻¹ (1st attempt) to 1.5 mg L⁻¹ (7th attempt). It could be concluded that one gram of PBP contains a total amount of 18.54 mg F which is about 14.3 times higher than the naturally existing granite powders with 200 – 1300 mg F per kg [10]. The three parameters namely F⁻, Ca²⁺ and TDS decreased gradually after every attempt and found to be proportional to one another (Fig. 7B).

4. Conclusions

Based on the above results and discussion, the following can be drawn. They are:

1. The characterization results of PBP ascertained the presence of basanite (CaSO₄. ½ H₂O), anhydrite CaSO₄, α- SiO₂ and carbon of 0.633% by mass.
2. Plaster board leaches the highest amount of fluoride at pH 6 of 3.7 mg L⁻¹.
3. The total amount of contained fluoride in 1 g of PBP was quantified to be 0.0185 g. The sodium forms of phosphate, carbonate and hydrogen carbonate were able to leach high amount of fluoride with no detectable calcium ions in water.
4. The stirring agitation was observed effective than shaking in view of leaching rate of fluoride and other ions encountered.

Acknowledgement

The authors thank Japanese Society for the Promotion of Science (JSPS) for the grant – in – aid for Scientific Research (L16544) and also Nagasaki University, Japan.

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