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A Suppression Method for Elution of F^- , $[B(OH)_4]^-$, AsO_4^{3-} , and CrO_4^{2-} from Industrial Wastes Using Some Inhibitors and Crushed Stone Powder

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Abstract: The disposal and the reuse of industrial wastes have become increasingly difficult due to the elution of hazardous anions, such as F^- , $[B(OH)_4]^-$, AsO_4^{3-} , and CrO_4^{2-} . Effective methods for removing hazardous ions and reusing solid wastes are urgently required. In this study, $Ca(OH)_2$, $MgCl_2$, and $BaCl_2$ were added to reduce the elution concentrations of F, B, As, and Cr by coprecipitating insoluble inorganic salts. After this, ordinary Portland cement (OPC) was added to the ion exchange and solidified with these hazardous ion-containing substances. The addition of crushed stone powder (CSP), which was a by-product of the process of crushing aggregates or sawing stone, inhibited the elution of hazardous ions and improved the inhibition effect of OPC. The elution concentrations of F, B, As, and Cr were successfully reduced from their maximum elution concentration of 10 mg/L to below the environmental standards values of Japan. A simultaneous inhibition method for the elution of F, B, As, and Cr from industrial wastes has been developed successfully and would be able to promote the reuse and recycling of CSP and other industrial wastes.

Keywords: hazardous anions; solidification; crushed stone powder

1. Introduction

Fluoride (F, F^-), boron (B, $[B(OH)_4]^-$), arsenate (As(V), AsO_4^{3-}), and chromium (Cr(VI), CrO_4^{2-}), which are eluted from industrial wastes, such as slag, incineration ash, and so on, are usually present as anions and oxyanions. The environmental standards of the Soil Contamination Countermeasures Law of Japan [1] stipulate that the maximum concentration values of F, B, As(V), and Cr(VI) are 0.8, 1.0, 0.01, and 0.05 mg/L, respectively. It is difficult to remove these harmful ions due to their high solubility. The disposal and the reuse of hazardous ion-containing industrial wastes have become increasingly important. In Japan, intermediate waste treatment, such as burning, crushing, and so on, has been carried out to reduce the quantity of the industrial wastes. However, there are still about 17.2 million cubic meters of wastes in 2014, which are left in landfills due to the presence of hazardous materials [2]. A stabilization/solidification (S/S) process using cement and other cementitious materials has become increasingly popular in the immobilization of hazardous ions and oxyanions [3–8]. The immobilization of wastes or contaminants has been reported that may involve the three following mechanisms: (a) chemical fixation of the contaminate, which occurs by chemical reaction between hydration products of the cement and the contaminate; (b) physical adsorption of the contaminate on the surface of the hydration products of the cements; and (c) encapsulation of the contaminate in the pores of the cement [8]. In addition, ettringite $[Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O]$, which is formed during the hydration

of ordinary Portland cement (OPC), showed a high removal preference for F [9–11], B [11–15], As [16,17], and Cr [12,18–21] due to its ion exchange capacity by replacing SO_4^{2-} of ettringite. In our previous study, F concentration eluted from CaF_2 pure reagent could be reduced from 288.5 mg/L to 0.47 mg/L in alkaline regions with the addition of $\text{Ca}(\text{OH})_2$, MgCl_2 , and OPC [22]. The coprecipitation effect of Ca^{2+} , ion exchange effect of ettringite, and solidification effect of Ca-bearing hydrates contribute to the decrease in the elution concentration of F. This has been successfully applied for the inhibition of F eluted from paper sludge and coal ash. This method allows treated fluorine-containing wastes to be applied as earth cover or road bed materials. We also studied the solidification/stabilization of arsenic in red mud and gypsum [23,24]. The As concentrations eluted from these wastes were successfully reduced to below the required environmental standards ($\text{As} \leq 0.01$ mg/L) using Fe(III) and/or Fe(II). The elution of As was reduced by forming insoluble Fe–As compounds, such as FeAsO_4 , using Fe(III), and/or Fe(II). Gypsum waste was successfully reused as a soil conditioner without arsenic contamination. However, this method was only carried out under weak acidic conditions and Fe–As compounds subsequently have a strong dependence on pH [25–28]. Moreover, there are usually many hazardous ions, such as F^- , $[\text{B}(\text{OH})_4]^-$, AsO_4^{3-} , and CrO_4^{2-} , that coexist in these industrial wastes. These hazardous ions usually need to be treated separately under certain conditions with different reagents, which further complicates the disposal and the reuse of industrial wastes. An effective method for the simultaneous suppression of these hazardous ions and the reuse of industrial wastes is urgently required.

Crushed stone powder (CSP) occurs as a waste by-product from the process of crushing aggregates or sawing stone. The generation rate of CSP during manufacturing processes was 1–25% [29–34]. This suggests that a considerable quantity of CSP would be generated in countries that are rich in the rock deposits, such as Portugal, Spain, and so on. It is difficult to utilize or dispose of this CSP because of its small grain size, the mixing of metals, and so on [31]. Therefore, it is generally disposed of in landfills. However, because of the continuous depletion of natural resources, the limited landfill land available, and increased transportation costs, there is a demand for the effective utilization of CSP. In recent years, there have been an increasing number of studies that focus on the recycling of CSP in concrete instead of in silica powder or sand [35–39]. However, further utilization of CSP in inhibiting the elution of hazardous ions is rarely found.

The aim of this study is to develop an effective method to suppress the elution of F^- , $[\text{B}(\text{OH})_4]^-$, AsO_4^{3-} , and CrO_4^{2-} from industrial wastes and to improve the reuse and recycling of CSP and other industrial wastes.

2. Materials and Methods

2.1. Materials

For the hazardous ions, the standard solutions of $[\text{B}(\text{OH})_4]^-$ (B 1000 mg/L), AsO_4^{3-} (As 1000 mg/L), and CrO_4^{2-} (Cr 1000 mg/L) were supplied by Kanto Chemical Co., Inc., Tokyo, Japan. F^- standard solution (1000 mg/L) was made from NaF (99.0%, Kanto Chemical Co., Inc., Japan). The additives, which were namely $\text{Ca}(\text{OH})_2$ (96.0%), $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (99.0%), FeSO_4 (99.0%), and BaCl_2 (99.0%), were supplied by Kanto Chemical Co., Inc., Japan. OPC was supplied by Sumitomo Osaka Cement Co., Ltd., Tokyo, Japan. CSP, which was derived from the Fukushima areas of Japan, was supplied by Kanno saiseiki Co., Ltd., Japan. The phase composition of CSP was characterized by X-ray diffraction. Chemical compositions and elution concentrations of the hazardous ions were determined according to the testing methods for industrial wastewater of Japan (JIS K 0102) [40] using ion chromatography and inductively coupled plasma mass spectrometer with lithium metaborate fusion method [41]. The equipment used in this study were a Perkin Elmer coupled plasma mass spectrometer (ICP-MS, ELAN DRC II, Kanagawa, Japan), Dionex ion chromatography (IC, DX-100, Tokyo, Japan), Shimadzu atomic absorption spectrophotometers (AAS,

AA7000HVG, Japan), Rigaku multipurpose X-ray diffraction spectrometer (XRD, Ultima IV, Tokyo, Japan), and Hitachi field emission scanning electron microscope (SEM, SU8000, Tokyo, Japan).

2.2. Methods

For the hazardous ions, a solution containing 200 mg/L of F, B, As, and Cr was made from 1000 mg/L of the abovementioned standard solutions of hazardous ions. A total of 5 mL of hazardous ions solution was mixed with 7 g of CSP, 3.0 g of OPC, 0.5 g of Ca(OH)₂, 0.4 g of MgCl₂, and 0.00, 0.10, 0.20, 0.30, and 0.40 g of BaCl₂. The mixed samples were stirred for 30 min with a stirring glass rod in a polypropylene bottle before being dried at room temperature for 48 h in a phenol culture dish ($\Phi = 85$ mm). The dried samples were crushed into a powder and subsequently placed in polypropylene bottles with water so that the water-to-sample ratio was 10:1. After this, they were shaken with a laboratory shaker (SA300, Yamato, Japan) at 200 rpm for 6 h before being filtered through 5C filter paper after centrifuging at 3000 rpm for 20 min with a low-speed centrifuge (LC-120, TOMY, Tokyo, Japan). The elution examination of dried samples was conducted according to the testing methods for industrial wastewater of Japan (JIS K 0102).

The pH measurements of the filtrates were obtained with a pH Meter (F-22, Horiba, Japan). The elution concentration of F was measured using IC. B and Cr were measured using ICP-MS. As was measured using AAS with a hydride generator. In addition, the crystal structure and phase composition of dried samples were characterized by XRD. The microstructures of the dried mixtures were examined using SEM.

3. Results and Discussion

The solutions of hazardous ions (200 mg/L) were added and mixed with CSP and OPC so that the maximum elution concentrations of these hazardous ions during elution examination were 10 mg/L in the case where all hazardous ions had been eluted.

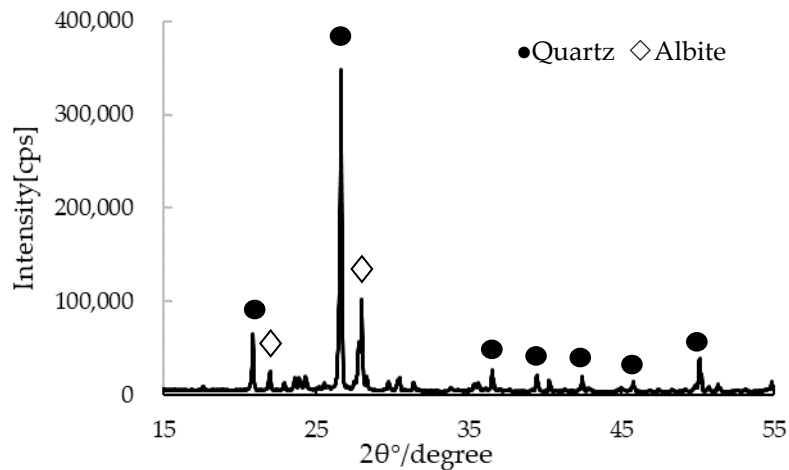
A decrease in the elution concentrations of F, B, As, and Cr was observed with an addition of CSP (Table 1). The elution concentrations of these hazardous ions were 7.15, 8.60, 2.75, and 4.46 mg/L (pH = 8.6), respectively, after the elution experiment. CSP is mainly comprised of components of quartz (SiO₂, File No. 01-046-1045) and albite (NaAlSi₃O₈, File No. 01-001-0739) (Figure 1). Furthermore, it has a high content of SiO₂ (52.9%) and Al₂O₃ (14.4%) (Table 2). In recent years, geopolymers as a type of alkali-activated aluminosilicates, such as calcium aluminosilicate hydrate and alkali aluminosilicate, was reported to immobilize hazardous ions [5,8,42,43]. Albite belongs to a type of sodium aluminosilicate. Geopolymer created from albite would form during the mixing of CSP and water. The forming of the geopolymer would greatly contribute to the immobilization of hazardous ions. The pH values of the filtrates of all the samples were above 12.2 with an addition of OPC. The inhibitory effects of OPC and CSP on the elution of F, B, As, and Cr are illustrated in Table 1.

Table 1. Experimental conditions and the elution concentrations of F, B, As, and Cr with additions of crushed stone powder (CSP) and/or ordinary Portland cement (OPC).

Sample No.	200 mg/L of Hazardous Ions Solution (mL)	CSP (g)	OPC (g)	Weight Ratio of OPC (wt.%)	Elution Conc. (mg/L)				pH
					F	B	As	Cr	
1	4.00	8.00	0.00	0	7.15	8.60	2.75	4.46	8.6
2	1.00	-	2.00	-	0.45	0.01	0.01	4.76	12.4
3	1.72	-	3.43	-	0.65	0.01	0.00	6.29	12.5
4	4.00	-	8.00	-	0.70	0.02	0.00	5.80	12.6
5	5.00	8.00	2.00	20	0.64	0.01	0.00	3.78	12.2
6	5.72	8.00	3.43	30	0.47	0.00	0.00	2.41	12.4
7	8.00	8.00	8.00	50	0.35	0.00	0.00	4.20	12.4

Table 2. Chemical compositions of CSP and elution concentrations of the hazardous ions by the testing methods for industrial wastewater of Japan (JIS K 0102).

Type of Material	Chemical Compositions (wt %)								Elution Conc. ($\mu\text{g/L}$)			
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Na ₂ O	MgO	K ₂ O	CaO	Other	F	B	As	Cr
CSP	52.9	14.4	2.1	3.2	0.6	1.2	2.9	22.6	82.0	0.6	0.0	2.6

**Figure 1.** XRD pattern analysis of CSP.

3.1. Suppression of F Elution

A significant decrease in the elution concentration of F was observed when only OPC was added. The elution concentration of F was reduced to 0.45 mg/L with an addition of 2.0 g of OPC, which was a value below its environmental standards ($F \leq 0.8$ mg/L). Portlandite ($\text{Ca}(\text{OH})_2$), calcium silicate hydrates (Ca_3SiO_5 and Ca_2SiO_4), and ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3\text{OH}_{12} \cdot 26\text{H}_2\text{O}$) are formed during the hydration of OPC. F could be reduced by coprecipitating CaF_2 [9] due to the high content of Ca^{2+} , which originates from cement hydrates. Our previous studies have shown that the solubility of CaF_2 increases with an increase in pH in the alkaline range due to the competition between F^- and OH^- [22]. However, ettringite with a high ion exchange capacity was formed during the hydration of OPC, and therefore, the elution of F was inhibited due to the replacement of the exchangeable anion, such as SO_4^{2-} in ettringite by F. The coprecipitation effect of Ca^{2+} , ion exchange effect of ettringite, and solidification effect of Ca-bearing hydrates contribute to the inhibition of the elution of F. Additionally, under the conditions of the same added amount of OPC, the elution concentrations of F were lower than those without additions of CSP. SiO₂ and Al₂O₃ in CSP could improve the solidification effect of Ca-bearing hydrates by becoming involved in the pozzolanic reaction. Furthermore, it is possible for CSP to react with OPC to generate calcium aluminosilicate hydrate and alkali aluminosilicate to immobilize F and other hazardous ions. Moreover, due to its small particle size, CSP could also fill in the gaps of cement paste, enhancing the density of the cement paste and improving the inhibitory effects of OPC.

The reflections assigned to quartz, albite, tricalcium silicate (Ca_3SiO_5 , ICSD file No. 00-055-0738), dicalcium silicate (Ca_2SiO_4 , ICSD file No. 00-039-0298), calcite (CaCO_3 , ICSD file No. 01-072-1937), and portlandite ($\text{Ca}(\text{OH})_2$, ICSD file No. 01-076-0571) were observed in the mixture with OPC and CSP OPC (Figure 2b). The generation of calcium aluminosilicate could not be confirmed by XRD, which is possibly due to the reflections assigned to calcium aluminosilicate being too weak to be seen. Ettringite with a high ion exchange capacity is a rod-like particle with 1–2 μm length. These particles were confirmed in the SEM images of the mixtures of OPC and the hazardous ions with/without an addition of CSP (Figure 3). Consequently, ettringite would form in the mixtures of OPC and the hazardous

ions with/without an addition of CSP. Hence, the coprecipitation effect of Ca^{2+} , ion exchange effect of ettringite, and solidification effect of Ca-bearing hydrates would contribute to the decrease in elution concentrations of these hazardous ions.

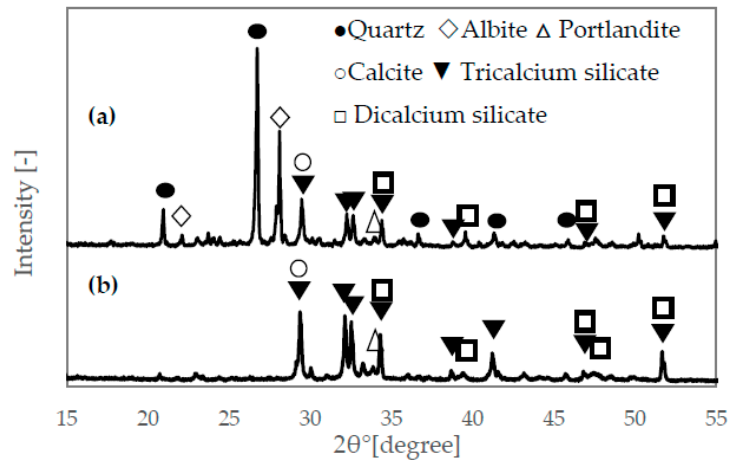


Figure 2. XRD patterns of hazardous ions mixed with 8.0 g of OPC (a) with CSP and (b) without CSP.

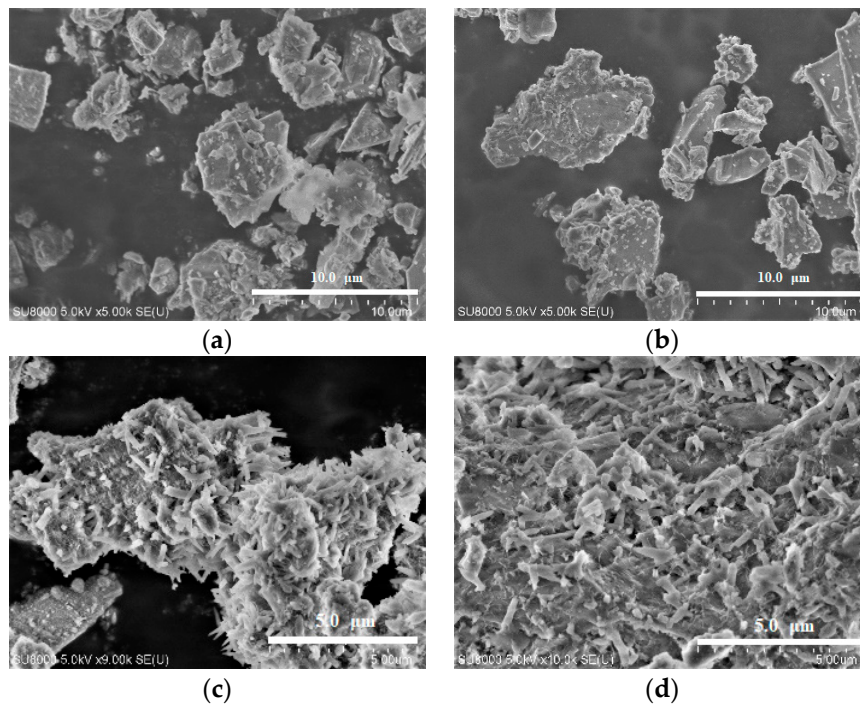


Figure 3. SEM images of (a) CSP and (b) OPC before reaction; and hazardous ions mixed with (c) 8.0 g of OPC and (d) 3.43 g of OPC and 8.0 g of CSP after reaction.

3.2. Suppression of B Elution

B was reported to be precipitated with $\text{Ca}(\text{OH})_2$ and OPC as calcium borate ($\text{CaO} \cdot \text{B}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$) [44–46]. The solution would become alkaline with an addition of OPC. B would be reduced by the formation of calcium borate. In this study, the elution concentration of B was reduced to 0.01 mg/L, which is far less than its environmental standards ($\text{B} \leq 1.0$ mg/L), with an addition of 2.0 g of OPC. The coprecipitation effect of Ca^{2+} , ion exchange capacity of ettringite, and solidification effect of Ca-bearing hydrates contribute to the inhibition of the elution of B. However, the coexistence of F and B possibly leads to the generation of BF_4^- , which further complicates the treatment of F and B [47]. In this study, the elution concentration

of BF_4^- was not detected by IC as the generation of BF_4^- requires certain conditions. The elution concentrations of F and B were all successfully reduced with an addition of OPC.

3.3. Suppression of As Elution

As could be reduced by forming insoluble Ca–As precipitates with Ca^{2+} [48–51], such as $\text{Ca}_3(\text{AsO}_4)_2 \cdot x\text{H}_2\text{O}$, $\text{Ca}_5(\text{AsO}_4)_3\text{OH}$, and $\text{Ca}_4(\text{OH})_2(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$. In alkaline regions, the dominant species of As(V) in solution are HAsO_4^{2-} and AsO_4^{3-} at $\text{pH} > 7$ (Figure 4). Zhu et al. studied the solubility and stability of calcium arsenates under different pH values [48]. The results showed that $\text{Ca}_3(\text{AsO}_4)_2 \cdot x\text{H}_2\text{O}$, $\text{Ca}_5(\text{AsO}_4)_3\text{OH}$, and $\text{Ca}_4(\text{OH})_2(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$ were identified in the experiment over a wide range of pH ($3.0 < \text{pH} < 13.4$) and for Ca/As molar ratios between 1.0 and 4.0. In this study, the elution concentration of As was reduced to 0.01 mg/L with an addition of 2.0 g of OPC. This elution concentration meets the environmental standards of As ($\text{As} \leq 0.01 \text{ mg/L}$). Due to the high content of Ca^{2+} originating from OPC, the elution of As was inhibited by the coprecipitation effect of Ca^{2+} , ion exchange capacity of ettringite, and solidification effect of Ca-bearing hydrates. Additionally, the presence of carbonate ($\geq 0.3 \text{ mol/L}$) would capture Ca^{2+} to generate CaCO_3 , suppressing the generation of Ca–As compounds and resulting in the release of As into the aqueous solution [51]. Therefore, the prevention of the carbonation of Ca^{2+} could be a way of promoting the inhibitory effect on As.

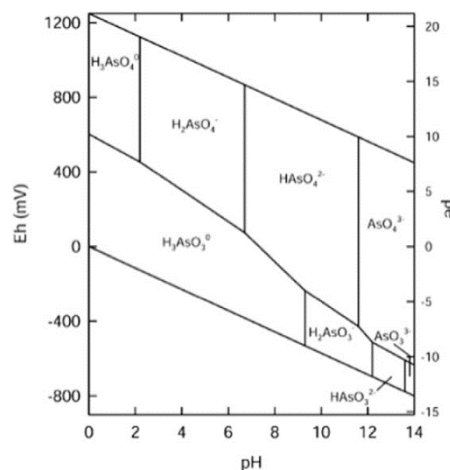


Figure 4. Eh–pH diagram for aqueous As species in the system As–O₂–H₂O at 25 °C and 1 bar total pressure. Referred from [52].

3.4. Suppression of Cr Elution

The immobilization of Cr(VI) by OPC was achieved due to the formation of the low solubility complex compounds, such as CaCrO_4 [53,54] and CrO_4 -ettringite. CaCrO_4 was formed by the reaction between Cr and Ca^{2+} at a high pH value. CrO_4 -ettringite was formed by the ion exchange between CrO_4^{2-} and SO_4^{2-} in ettringite. Some researchers studied the inhibitory effect of calcium silicate hydrate on Cr [55–57]. In the study of Zhang et al., in terms of calcium silicate hydrate (C–S–H), one of the most important hydration products of OPC, it seemed that the chemical incorporation degree of Cr(VI) was relatively low and just a sorption mechanism was more possible [21]. In this study, although the elution concentration of Cr decreased with an addition of OPC, it was still higher than its environmental standards ($\text{Cr} \leq 0.05 \text{ mg/L}$).

$\text{Ca}(\text{OH})_2$, MgCl_2 , and BaCl_2 were added to decrease the quantity of eluted Cr by forming insoluble salts. The addition of $\text{Ca}(\text{OH})_2$ results in a reduction in the elution of F, B, As, and Cr. MgCl_2 was able to prevent the carbonation of Ca^{2+} [58,59] and coprecipitate with F and B to create MgF_2 and $\text{Mg}[\text{B}(\text{OH})_4]_2$. BaCl_2 could suppress the elution of Cr by coprecipitating into the form of BaCrO_4 [60].

Additionally, As could also react with Ba^{2+} to form the insoluble salt $\text{Ba}_3(\text{AsO}_4)_2$ ($K_{\text{sp}} = 2.59 \times 10^{-9}$, 20°C), which is stable within the pH range of 12–14 [61]. FeSO_4 was added to compare the inhibitory effect on Cr with BaCl_2 .

The pH values of the filtrates of all the samples were above 12.1 with the additions of CSP, OPC, $\text{Ca}(\text{OH})_2$, MgCl_2 , and BaCl_2 . The elution concentration of Cr decreased significantly with these additives and further decreased with an increase in the added amount of BaCl_2 (Figure 5). When 0.2 g of BaCl_2 was added, the Cr elution concentration was reduced to 0.01 mg/L, which is below its environmental standard value. In contrast, the lowest elution concentration of total Cr, which was in the forms of Cr(VI) and Cr(III), was 0.14 mg/L with an addition of FeSO_4 . BaCl_2 is obviously superior to FeSO_4 in reducing the elution of Cr in this study. On the one hand, FeSO_4 inhibited Cr(VI) by reducing it to Cr(III). This process was generally carried out under acidic conditions. Otherwise, Fe(II) would react with OH^- to form $\text{Fe}(\text{OH})_2$ before oxidizing in the air to form $\text{Fe}(\text{OH})_3$ and weakening its reduction ability. Moreover, Cr(VI) could be separated from Fe(II) by the generation of floccules, which are namely $\text{Fe}(\text{OH})_2$ and/or $\text{Fe}(\text{OH})_3$, resulting in a decrease in the inhibiting effect on Cr [62]. On the other hand, additional operations are required to suppress Cr(III) after reduction reaction. Therefore, the treatment of Cr by BaCl_2 was simpler and more effective than FeSO_4 . In addition, it was easy to react BaCl_2 with SO_4^{2-} to generate the insoluble salt BaSO_4 ($K_{\text{sp}}, \text{BaSO}_4 = 2.45 \times 10^{-4}$, 20°C) due to its low solubility. This would lead to a reduction in the amount of SO_4^{2-} of gypsum, which plays an important role in the composition of ettringite, resulting in the suppression of the hydration of OPC [63,64]. Therefore, the added amount of BaCl_2 should be controlled. In this study, the elution concentrations of F, B, and As were 0.20, 0.18, and 0.00 mg/L, respectively, with additions of CSP, OPC, $\text{Ca}(\text{OH})_2$, MgCl_2 , and 0.2 g of BaCl_2 , while there were no obvious changes with an increase in the added amount of BaCl_2 . The elution concentrations of F, B, As, and Cr were successfully inhibited to be lower than the environmental standards values with additions of CSP, OPC, $\text{Ca}(\text{OH})_2$, MgCl_2 , and 0.2 g of BaCl_2 .

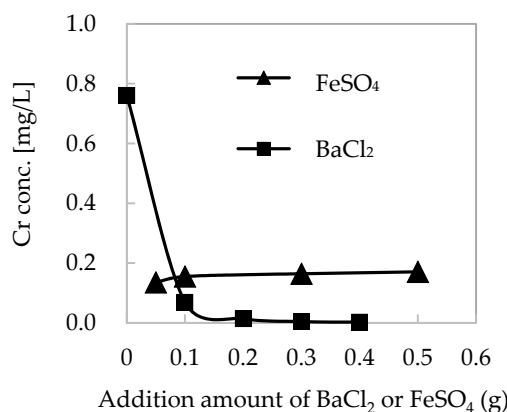


Figure 5. The elution concentrations of Cr with additions of 7.0 g of CSP, 3.0 g of OPC, 0.5 g of $\text{Ca}(\text{OH})_2$, 0.4 g of MgCl_2 , and a certain amount of BaCl_2 and FeSO_4 .

4. Conclusions

The elution concentrations of F, B, As, and Cr were successfully reduced from their maximum elution concentrations of 10 mg/L to below the environmental standards values with the additions of $\text{Ca}(\text{OH})_2$, MgCl_2 , BaCl_2 , OPC, and CSP. Metal salts reduced the elution concentrations of F, B, As, and Cr by coprecipitation into insoluble inorganic salts. After this, OPC was added to the ion exchange and solidified with these hazardous ion-containing substances. The addition of CSP inhibited the elution of hazardous ions and improved the inhibition effect of OPC. A simultaneous inhibition method for the elution of F, B, As, and Cr from industrial wastes has been developed successfully and would be able to promote the reuse and recycling of industrial wastes.

Author Contributions: A.S. and X.K. performed the experiments; X.K. wrote the paper; and A.S. and M.E. reviewed and edited the manuscript. M.E. supervised the findings of this work. All authors discussed the results and contributed to the final manuscript.

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