Practice and design of the self-purification system for heavy metals-bearing contaminants

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Abstract: Many minerals in nature have self-purification capacity to hold and stabilize deleterious contaminants into their lattice structures, which can be used for treatment of heavy metals-bearing contaminants. Hydrotalcite Layer Double Hydroxide (LDH), tobermorite Calcium Silicate Hydrate (CSH) and apatite are ubiquitous minerals in nature, having higher geochemical stability and potential for binding and stabilizing heavy metals. Based on the elucidation of crystal structure property and self-purification principles of the three minerals above, this article discussed how to design the self-purification system of heavy metal-bearing contaminants.

Key words: self-purification; LDH; CSH; apatite; heavy metals

1 Introduction

Heavy metals-bearing contaminants are a large group of hazardous wastes, and the safety landfill is a principle option for safe disposal of hazardous wastes after pretreated by physical and chemical immobilization. Good leaching resistance, low compatibilization ratio, cheap and easily available immobilization materials, and simple and convenient immobilization technology are all basic principles for designing and choosing immobilization materials.

The immobilization using cement is a traditional and basic method for pretreatment of inorganic heavy metals-bearing contaminants, which immobilizes heavy metals by physical and chemical adsorption, formation of heavy metal hydrates, exchange of lattice ions, and so on. However, traditional cement immobilization may cause high compatibilization, higher porosity and higher permeability. Moreover, the binding effectiveness to some amphoteric cations such as Zn^{2+}, Pb^{2+} and high valent of heavy metal anion groups such as CrO_4^{2-} is not as expected under high alkaline condition of $pH > 12.5$. Meanwhile, the precipitation of heavy metal hydrates can immobilize heavy metals, whereas, the pH conditions in which the hydrates of various heavy metals attain theoretic minimum solubility vary considerably from each other. If pH of the solution deviates from the pH of minimum solubility of hydrate, the trend of dissolution for hydrate may increase. Therefore, it is difficult for traditional cement immobilization system to co-precipitate different heavy metals forming geo-chemically stable heavy metal hydrates.

According to the demands for treatment and disposal of hazardous contaminants, it is a new field to seek for new solidification/stabilization pretreatment method to improve the stability and reduce the compatibilization ratio of heavy metal precipitations. In 1990, Shuiling, for the first time, proposed the geochemical engineering theory that used the idea of geochemical activities to solve the self-purification of different environment contaminants[1]. The geochemical engineering simulates the various self-purification activities in nature, emphasizing the use of natural geochemical process, avoiding interference with the nature and choosing the materials in situ, removing and self-purifying the deleterious chemical elements depending on element recycle, with the aim of improving the human living environment, but don't bring new pollution.

The theory of geochemical engineering illuminates us that many minerals in nature have special crystal structures similar to natural reservoir with great self-purification capability of holding and stabilizing deleterious substances. The potential for self-purification rests with the adsorption on surface of minerals, the filtration of porous, structure adjustment, ion exchange, chemical activity, physical effect, nanometer effect, biological interaction, and so on[2]. Therefore, it is a new concept to build a new system for treating hazardous contaminants by adjusting the compositions and forming environment of pollutant treatment system to the situation with similar formation paths and formation conditions of natural self-purification minerals in order

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to realize the self-bound and stabilization of pollutants.

Based on the property of pollutants and complicated ambient medium, the selection of self-purification minerals must have the characteristics of easily-formed, low solubility, low leaching ratio, high pH stability, high bound ability to various heavy metal cations and anion groups. Mg-Al hydrotalcite, hydrocalumite, tobermorite Calcium Silicate Hydrate (CSH) and apatite are all clay-like mineral phases easily available in nature. The existed fundamental researches have substantiated that the constituent and structure of these minerals can induce heavy metals-bearing hazardous waste to form pollutants-bearing self-purification systems. Based on the lattice structure of minerals and self-purification principles, this article took the three systems hydrotalcite Layer Double Hydroxide(LDH), tobermorite CSH and apatite for example, briefly discussed the effectiveness of them in self-purification of hazardous contaminants, providing certain theoretic foundation for the design of self-purification system for hazardous pollutants.

2 Hydrotalcite-like LDH system

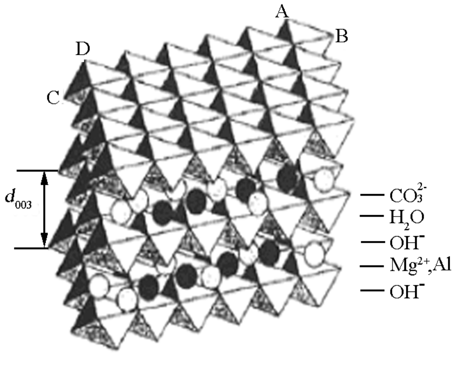
Hydrotalcite-like Layer Double Hydroxide systems can be divided into Mg-Al hydrotalcite system and hydrocalumite system, and both of them have the layer structure of Mg-Al hydrotalcite.

Mg-Al hydrotalcite is a kind of layer mineral ubiquitous in natural soil. As both basic constituent and structure cell of it, heavy metal can be bounded in its layer structure[3], such as $Mg_6Mn_2(OH)CO_3 \cdot 4H_2O$, $Ni_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$, $Mg_6Cr_2(OH)_{16}CO_3 \cdot 4H_2O$, $Ni_6Fe_2(OH)_{16}CO_3 \cdot 4H_2O$, $Ni_xCo_{(1-x)}(OH)_2(CO_3)_{(1-x)/2} \cdot nH_2O$, etc[4-6]. Due to the formation of carminite ($Pb(Fe^{3+})_2(AsO_4)_2(OH)_2$), pharmacosiderite ($K(Fe^{3+})_4(AsO_4)_3(OH)_4 \cdot (6\sim7)H_2O$), talmessite ($Ca_2Mg(AsO_4) \cdot 2H_2O$) and so on, containing As-Mg-Al hydrotalcite structure in soil contaminated by arsenic, the leaching toxicity of arsenic in soil is inhibited. The chromium pollution caused by residue of chromite is an important issue about global environmental pollution. Under high alkaline condition, the soil polluted by chromite can form minerals of layer structure containing chromium, such as chromium-hydrocalumite ($Ca_4(AlFe)_2(OH)_{12}CrO_4 \cdot 6H_2O$), chromium-calcia-carnotite ($Ca_6Al_2(OH)_{12}(CrO_4)_3 \cdot 26H_2O$) etc., decreasing the toxic risk of chromium to ambient environment effectively. At the same time, in fly ash, leachate of oil shale residue and hydration products of Portland cement, the hydrocalumite ($3CaOAl_2O_3Ca$) phase is also the main mineral system containing Cd^{2+}, Zn^{2+}, Ni^{2+}, Mn^{2+}, Co^{2+}, $B(OH)^{4-}$, CrO_4^{2-}, MoO_4^{2-}, SeO_4^{2-} and so on.

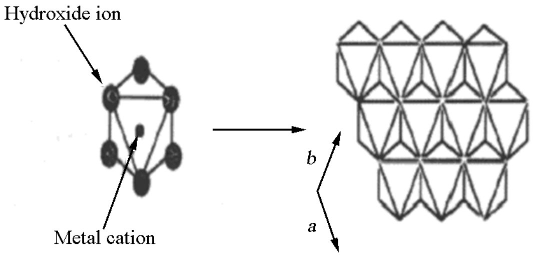
2.1 Mg-Al hydrotalcite-like LDH system

2.1.1 The crystal structure property of Mg-Al hydrotalcite-like LDH system

The compounds of Mg-Al hydrotalcite-like LDH system have layer structures of natural hydrotalcite. The natural hydrotalcite is a kind of mineral ubiquitous in nature, which is mainly Mg-Al hydrotalcite, and the layer anion is mainly CO_3^{2-}. Fig. 1 shows the three-dimensional structure of hydrotalcite, where Fig. 1 (a) is layer structure schematic diagram, and Fig. 1 (b) is the arrangement of hydroxide ion in octahedron. Natural hydrotalcite-like clay minerals are of layer structure similar to brucite. In the layer structure of brucite, every Mg^{2+} is surrounded by six OH^-, forming an octahedron structure, then many octahedrons use a common side and stretch for two directions forming a huge layer. When the metal ion M^{2+} in layer structure is substituted by M^{3+}, structural positive charge emergences, and anion need to be introduced into the cell layer structure to equilibrize the structural positive charge, thereafter, the layer two-hydroxide LDH structure formed. The basic formula of it is $[M^{2+}_{(1-x)}M^{3+}_x(OH)_{2x}]^{x+}(A^{n-})_{x/n} \cdot mH_2O$, where M^{2+} represents divalent cations, including Mg, Fe, Mn, Zn, Co, Ni, Cu, etc.; M^{3+} represents trivalent cations, such as Fe, Co, Mn, etc.; A is anion, including NO_3^-, Cl^-, F^-, OH^-, MoO_4^{2-}, SO_4^{2-},



(a) Crystal structure of hydrotalcite



(b) The arrangement of hydroxide ion in octahedron

Fig. 1 Schematic diagram of the three-dimensional structure of hydrotalcite[7]

CrO_4^{2-}, CO_3^{2-}, etc.

As known from the formula of LDH, the constituents of LDH can be adjusted in a wide range, that's to say, the constituent species can be varied and the ratio can be regulated. Furthermore, the anions or anion groups in the layer can change mutually and easily. It is just the structural characteristic of LDH that favors the heavy metal ions finding places for themselves and existing in LDH steadily. Hydrotalcite is a kind of natural mineral self-formed in nature; therefore, the isomorphous substitution phenomenon widely existed in it. Table 1 lists partial compounds of LDH structure. Given the crystal structure property of hydrotalcite-like LDH system combined with the chemical composition of contaminants, it is of vital scientific significance that immobilizing heavy metal ions in the lattices of LDH compounds in the self-forming process by certain means and then realizing the self-purification of pollutants.

Table 1 Some LDH mineral groups with different heavy metals

Commom name	Chemical composition	Commom name	Chemical composition
Hydrotalcite	$Mg_6Al_2(OH)_{16}CO_3\cdot 4H_2O$	Coalingite	$Mg_{10}Fe_2(OH)_{24}CO_3\cdot 2H_2O$
Manasseite	$Mg_6Al_2(OH)_{16}CO_3\cdot 4H_2O$	Meixnerite	$Mg_6Al_2(OH)_{18}\cdot 4H_2O$
Pyroaurite	$Mg_6Fe_2(OH)_{16}\ CO_3\cdot 4.5H_2O$	Brugnatellite	$Mg_6Fe(OH)_{13}CO_3\cdot 4H_2O$
Sjorenite	$Mg_6Fe_2(OH)_{16}\ CO_3\cdot 4.5H_2O$	Honessite	$Ni_6Fe_2(OH)_{16}SO_4\cdot 4H_2O$
Stichtite	$Mg_6Cr_2(OH)_{16}\ CO_3\cdot 4H_2O$	Woodwardite	$Cu_4Al_2(OH)_{12}\ SO_4\cdot 4H_2O$
Barbertonite	$Mg_6Cr_2(OH)_{16}\ CO_3\cdot 4H_2O$	Zincowoodwardite	$Zn_{0.47}Al_{0.38}(OH)_2(SO_4)_{0.18}\cdot 4H_2O$
Takovite	$Ni_6Al_2(OH)_{16}CO_{3}\_OH\cdot 4H_2O$	Hydrowoodwardite	$Cu_{0.5}Al_{0.5}(OH)_2(SO_4)_{0.25}\cdot 4H_2O$
Reevsite	$Ni_6Fe_2(OH)_{16}\ CO_3\cdot 4H_2O$	Iowaite	$Mg_4Fe(OH)_{10}Cl\cdot 3H_2O$
Desautelsite	$Mg_6Mn_2(OH)_{16}CO_3\cdot 4H_2O$	Woodallite	$Mg_6Cr_2(OH)_{16}Cl_2\cdot 4H_2O$
Motukoreaite	$NaMg_{19}Al_{12}(OH)_{54}(CO_3)_{6.5}(SO_4)_4\cdot 28H_2O$	Mountkeithite	$Mg_{8.1}Ni_{0.9}Fe_{1.3}Cr_{1.0}Al_{0.6}(OH)_{24}(CO_3)_{1.1}$ $(SO_4)_{0.4}Mg_{1.8}Ni_{0.2}(SO_4)_{1.9}$
Wermlandite	$Mg_7AlFe(OH)_{18}Ca(SO_4)_2\cdot 12H_2O$	Hydrohonessite	$Ni_{5.43}Fe_{2.57}(OH)_{16}\cdot 6.95H_2O(SO_4)_{1.28}$ $\cdot 0.98NiSO_4$
Chlormagaluminite	$Mg_{3.55}Fe_{0.27}Na_{0.05}Al_{1.93}Fe_{0.07}Ti_{0.01}(OH)_{12}Cl_{1.48}$ $(0.5CO_3)_{0.24}\cdot 2H_2O$	Carrboydite	$(Ni,Cu)_{6.90}Al_{4.48}(OH)_{21.69}$ $(SO_4,CO_3)_{2.78}\cdot 3.67H_2O$

2.1.2 The application of Mg-Al hydrotalcite-like LDH system

LDH has wide exchangeable range in layer anions which can exchange with various anions, including Cl^-, SeO_3^{2-}, SO_4^{2-}, $Cr_2O_7^{2-}$, CrO_4^{2-}, AsO_4^{3-}, VO_4^{3-}, $V_2O_7^{4-}$, PO_4^{3-}, IO_3^-, $W_7O_{24}^{6-}$, etc. In the self-forming process of LDH, various polluting anions are immobilized in their lattice structure, therefore, the self-purification of waste water system can also be expected to realize by inducing the self-forming of LDH.

Using the synthesizing principle of LDH as reference, Chen et al. proposed a new method of synthesizing layer hydroxides and removing anions simultaneously[8]. In the waste water treatment process, when Mg^{2+}, Al^{3+} hydrolyzes, co-precipitates, and LDH forms, the anion group CrO_4^{2-}, anion dye congo red and so on can enter into the layer structure preferentially to equilibrize the structural charge, then these anions or anion groups are removed efficiently as LDH precipitation.

Saber et al. synthesized Zn-Ti LDH, Co-Ni LDH and Ni-Al LDH by simulating waste water system and inducing the self-forming of LDH[9-11]. Kameda et al. treated the heavy metals Cu and Cd adopting method of synthesizing hydrotalcite, finding that in the solution of pH 5 Cu and Cd can be adsorbed into the layer of Mg-Al hydrotalcite and the removal efficiency is over 95 %[12].

It is demonstrated that CO_3^{2-} is the most stable anion group in LDH mineral lattice and also the major constituent of LDH; moreover, LDH compounds can steadily exist in a quite wide pH range. Frost et al. synthesized and characterized Cu-LDH compound $Cu_xZn_{(6-x)}Cr_2(OH)_{16}(CO_3)\cdot 4H_2O$ that can be used as catalyzer by co-precipitation method for the first time[13]. Taking $Cu_xZn_{(6-x)}Cr_2(OH)_{16}(CO_3)\cdot 4H_2O$ as target mineral, we regulated and induced the self-forming of CuZnCr-LDH-like layer compounds by means of accelerating carbonization via CO_2[14]. The primary research demonstrated that the formed product was new LDH compounds which were characterized by layer structure, and was inferred to be

$$[(Cu^{2+}Zn^{2+}Ni^{2+})_{(1-x)}Cr_x^{3+}(OH)_{2x}]^{x+}(CO_3)_{(x/n)}\cdot mH_2O.$$

Furthermore, the removing rate of Ni, Zn, Cu and Cr arrived at 99 % after carbonization, which was better than the effect of adding lime, and the quantity of secondary waste sludge almost can be ignored.

In addition, due to the exchangeable property of layer anions and the memory effect after calcination and superficial adsorption, the LDH compounds can also be used for removing organic pollutants phenol, pesticides, surfactant and acid organic compounds[15]. Moujahid et al. synthesized styrene sulfonate, poly-styrene sulfonate, amino-benzenesulfonic salt and polymethyl methacrylate by synthesizing LDH in situ[16].

2.2 Hydrocalumite-like LDH system

2.2.1 The crystal structure property of Hydrocalumite-like LDH system

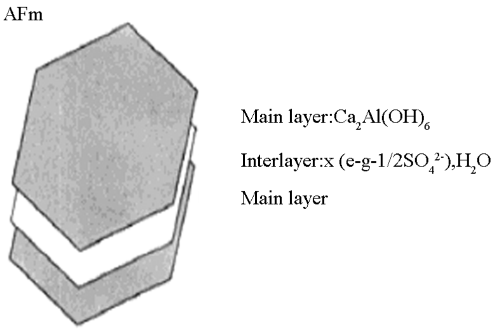
Natural Hydrocalumite was firstly found in England in 1934. Hydrocalumite-like LDH system is also named as AFm (Aluminate Ferrite mono-) family mineral, having similar layer structure with hydrotalcite. AFm family mainly includes hydrated calcium aluminate, the AFm phase $CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 10H_2O$, hydrated calcium chloroaluminate, the Friedel's salt phase $3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O$ and hydrated car bon calcium aluminate phase $3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 10H_2O$. The three kinds of phases mentioned above are all solid solutions of layer structure, and the structural cell is composed of major positive charge layer $[Ca_2Al(OH)_6]^+$ and middle negative charge layer $[0.5X \cdot H_2O]^-$($X = Cl^-$, OH^-, SO_4^{2-}, CO_3^{2-} and so on)[17]. Fig. 2 shows the schematic diagram of AFm family compounds.

The bound of AFm family compounds to heavy metals is mainly via the ion exchange of lattice. Plenty of researches indicated that $B(OH)_4^-$, CrO_4^{2-}, MoO_4^{2-}, SeO_4^{2-}, SO_3^{2-} can substitute the anion in the middle layer of AFm family compounds, the Al^{3+} in the major layer can be substituted by Cr^{3+}, Mn^{3+} and Ti^{3+}, and the Ca^{2+} can be substituted by Cd^{2+} of similar ion radius[18,19].

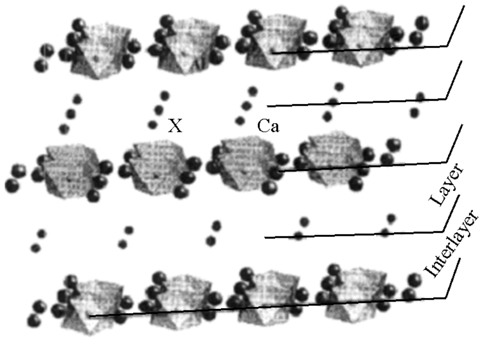
2.2.2 Application of Hydrocalumite-like LDH self-purification system

As a major targeting product in hazardous pollutants self-purification system, Segni et al. synthesized hydrocalumite with substitution of Cr and Se[20,21]. By simulating the formation of hydrocalumite by co-precipitation, Zhang et al. removed anion groups $B(OH)_4^-$, SeO_4^{2-}, CrO_4^{2-}, and MoO_4^{2-} in waste water system[22]. The results showed that anion groups $B(OH)_4^-$, SeO_4^{2-}, CrO_4^{2-}, and MoO_4^{2-} entered into the lattice structure of hydrocalumite by co-precipitation. The concentration of anion groups in the waste water treated by this method can meet the standard for drinking water.

Friedel's salt $Ca_2Al(OH)_6Cl(H_2O)_2$, hydrated calcium chloroaluminate, is a member of AFm family. Auer synthesized Cd-Friedel's salt based on substitution of Ca^{2+}[23]. Researches also indicated that **some heavy metal anion groups like CrO_4^{2-}**, $B(OH)_4^-$ and AsO_4^{2-} can substitute the anion groups located in the middle negative charge layer. According to the Friedel's salt property of hydrotalcite-like layer structure, it is expected that Friedel's salt is a potential compound that can stabilize heavy metal ions effectively.



(a) Crystal structure of AFm phase



(b) Compound structure of AFm family

Fig. 2 Schematic representation of the three dimensional structure for hydrotalcite[7]

Cao researched the possible restraining and stabilization mechanism of typical heavy metal Se, V, Cr, Pb and Zn in immobilization matrices, and found that not only the lattice cations Ca^{2+} and Al^{3+} can exchange with heavy metal cations Pb^{2+}, Zn^{2+}, Cr^{3+} and attain stabilization, forming $6PbO \cdot PbCl$, $Pb_2OCl(OH)$, $(Zn_{0.667}Al_{0.333})_2(OH)_4(CO_3)_{0.333}(H_2O)$, $Ca(Zn(OH)_3)_2 \cdot 2H_2O$and $Cr_2(OH)_6(H_2O)_4$, but also the chloride ion in the lattice can exchange with anion groups CrO_4^{2-}, $Cr_2O_7^{2-}$ and SeO_4^{2-}, forming new compounds $3CaO \cdot Al_2O_3 \cdot CaCrO_4 \cdot 14H_2O$, $Ca_6Al_2(SeO_4)_3(OH)_{12} \cdot 26H_2O$, while VO_4^{3-} is adsorbed by Friedel's salt[24].

Using Municipal Solid Waste (MSW) fly ash as immobilizing raw material, Qian et al. co-treated industrial heavy metal sludge and found that the immobilizing rate of immobilization system to heavy metals can be over 99 %[25]. Friedel's salt is a main mineral phase in immobilization system, playing a vital role in restraining and immobilizing heavy metals.

3 Tobermorite-like CSH system

Tobermorite $Ca_5Si_6O_{16}(OH)_2 \cdot 4H_2O$ is a natural mineral, symbiotic with carbonatite in metasediment, having similar crystal structure property with carbonatite, that is huge reservoir and layer structure. Tobermorite is acknowledged as an important natural cation exchanger. The main hydrate product of traditional cement immobilization matrix is CSH phase, with common layer structure with tobermorite. CSH phase can immobilize and stabilize heavy metals Cr^{6+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Hg^{2+} and radioactive elements Sr, Cs in its lattice.

3.1 The crystal structure property of CSH system

CSH phase is the main mineral phase in cement immobilization matrix. CSH has nano-layer structure, adsorbing masses of water molecules on the surface of particles, and the specific surface area is as high as 44 ~49 m^2/g, which determines the strong physical and chemical adsorption capacity of CSH to heavy metals. Fig. 3 shows the nano-structure diagram of CSH gel, thereof the grey layer substances present CSH particles, while the white points present the water molecules adsorbed on it.

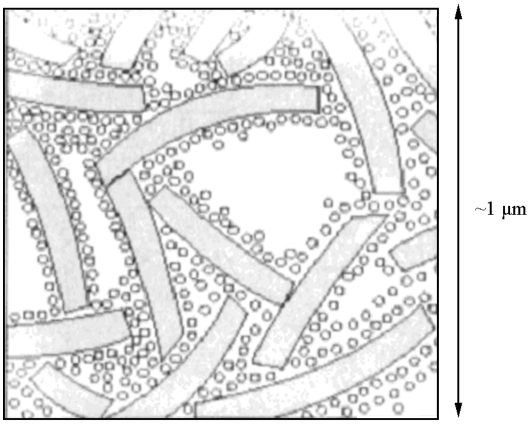


Fig. 3 Hypothetical reconstruction of the nano-structure of CSH gel[26]

In the forming process of CSH, some low valent heavy metal ions, such as Cd^{2+} and Cu^{2+} can compete with Ca^{2+} and enter into the lattice of CSH preferentially. The restrain of CSH phase to heavy metals depends on adsorption and ion exchange, and low Ca/Si ratio favors the adsorption of heavy metal cations. At present, the possible ions existing in CSH phase steadily mainly include Li^+, Na^+, K^+, Rb^+, Cs^+, Mg^{2+}, Ni^{2+}, Co^{2+}, Hg^{2+}, Zn^{2+}, Cd^{2+}, Cu^{2+}, Al^{3+}, Fe^{2+}, Cr^{3+}, Pb^{2+}, U^{2+}, Cl^-, I^-, OH^-, CO_3^{2-} and SO_4^{2-}. Hence, in the self-forming process of CSH, inducing heavy metals entering into the lattice structure of CSH preferentially can realize the self-purification of pollutant system.

3.2 Application of CSH self-purificati on system

Alkali-activated slag(AAS) binding material is a kind of new immobilization matrix, CSH as predominant phase, which is of property that low Ca/Si ratio and high alkaline, favoring the immobilization of heavy metals. Deja researched the effect of heavy metals Cr^{6+}, Cd^{2+}, Pb^{2+} and Zn^{2+} on hydrating of alkali-activated slag, pointing out that CSH was the main hydration product, and the immobilization ratio of heavy metals Cr^{6+}, Cd^{2+}, Pb^{2+} and Zn^{2+} arrived at 99 %[27].

Qian et al. studied the immobilization and stabilization of Alkali-activated slag system to heavy metals Hg and Zn, finding that Hg and Zn all entered into the lattice of CSH[28,29].

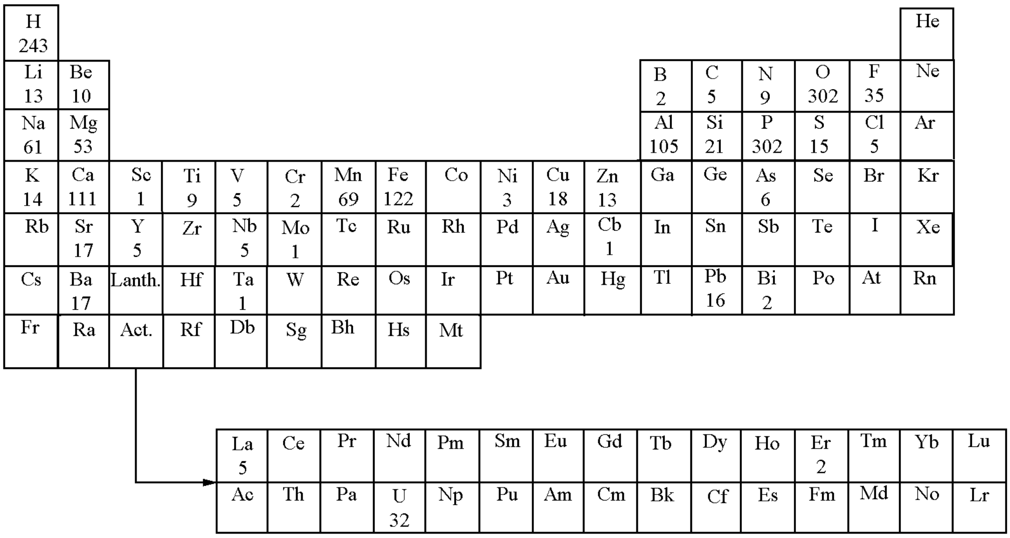
Hydrated calcium silicate not only has good immobilizing effectiveness on heavy metals, but also the restrain of it to radioactive elements is a research issue on the application of AAS binding material. Qian et al. found that alkali-activated slag system rich of Al had good preferable selective adsorbing ability for Sr and Cs, and the hydration products were mainly CSH phase substituted by Na^+ and Al^{3+}[30]. Shrivastave et al. researched the selective adsorption of radioactive element Cs using hydrated calcium silicate substituted by Na^+ and Al^{3+}, and observed that hydrated calcium silicate substituted by Na^+ and Al^{3+} had high ion exchange capacity, with strong adsorption effect on Cs[31].

4 Apatite system

There are many kinds of secondary phosphate minerals weathering from apatite existing in nature, containing various heavy metals Cu^{2+}, Pb^{2+}, Cd^{2+}, Zn^{2+} and so on, with high geochemical stability. $PbAl(PO_4)_2(OH)_5H_2O$, $Pb_5(PO_4)_3Cl$, $(Ca,Cd)_5(PO_4)_3OH$, $(Ca,Zn)_5(PO_4)_3OH$, $CuAl_6(PO_4)_4(OH)_8 \cdot 4H_2O$, $Zn_2(PO_4)OH$, $Cu_2(PO_4)OH$, $CuFe_6^{3+}(PO_4)_4(OH)_3 \cdot 4H_2O$, $LiAl(PO_4)F$ are all phosphate minerals ubiquitous in soil.

4.1 The crystal structure property of apatite family mineral

Phosphate type is various, and there are more than 30 kinds of elements reacting with $[PO_4]$, forming more than 300 kinds of stable phosphate minerals mainly existing in soil and sediments. Fig. 4 lists the element species in phosphate minerals and the quantity of minerals containing these elements. Therefore, using apatite family minerals $Ca_5(PO_4)_3OH$, $(Ca,Cd)_5(PO_4)_3OH$, $(Ca,Zn)_5(PO_4)_3OH$, $Pb_5(PO_4)_3Cl$ for immobilizing and stabilizing hazardous pollutants are research field of concerns.



H 243																	He
Li 13	Be 10											B 2	C 5	N 9	O 302	F 35	Ne
Na 61	Mg 53											Al 105	Si 21	P 302	S 15	Cl 5	Ar
K 14	Ca 111	Sc 1	Ti 9	V 5	Cr 2	Mn 69	Fe 122	Co	Ni 3	Cu 18	Zn 13	Ga	Ge	As 6	Se	Br	Kr
Rb	Sr 17	Y 5	Zr	Nb 5	Mo 1	Tc	Ru	Rh	Pd	Ag	Cb 1	In	Sn	Sb	Te	I	Xe
Cs	Ba 17	Lanth.	Hf	Ta 1	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb 16	Bi 2	Po	At	Rn
Fr	Ra	Act.	Rf	Db	Sg	Bh	Hs	Mt									

La 5	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er 2	Tm	Yb	Lu
Ac	Th	Pa	U 32	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Fig. 4 The types of elements existing in naturally occurring phosphate minerals and quantities of minerals containing these elements[32]

Apatite is a kind of phosphate minerals which is found the earliest and richest reserves. The phosphorus in nature mainly exists in form of apatite, whose formula is $M_{10}(PO_4)_6Y_2$, where M is divalent ions represented by Ca^{2+}, Mg^{2+}, Fe^{2+}, Sr^{2+}, Mn^{2+}, Pb^{2+}, Cd^{2+}, Zn^{2+}, Ba^{2+} and so on; ${PO_4}^{3-}$ can be substituted by ${AsO_4}^{3-}$, ${SO_4}^{2-}$, ${SiO_4}^{2-}$, ${CO_3}^{2-}$, ${VO_4}^{3-}$, ${CrO_4}^{2-}$ etc.; Y is mainly anion, such as OH^-, F^-, Cl^-, etc[33]. Fig. 5 shows the projective structure diagram of apatite in 001 side, and Fig. 6 shows the channel structure diagram of apatite.

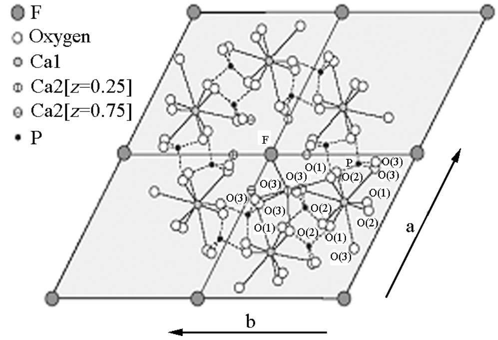


Fig. 5 The projective structure diagram of apatite in 001 side[34]

There are two types of ligand places for Ca, Ca1 and Ca2 locations; therefore, there are two kinds of structure channels in apatite crystal structure: the limited channel formed by Ca1 location with nine ligands and [PO_4], and the expanded channel formed by Ca2 location with six or seven ligands and [PO_4]. Then, the additional anions OH^-, F^- and Cl^- will fill in the channels. The structure property of apatite results in its isomorphous substitution by many kinds of cations or anions, not changing the crystal structure. Due to the broad cation or anion substitution property of apatite minerals and high geochemical stability, it makes great contributions to the field of self-purification of hazardous pollution. Table 2 lists the K_{sp} of partial apatite family minerals.

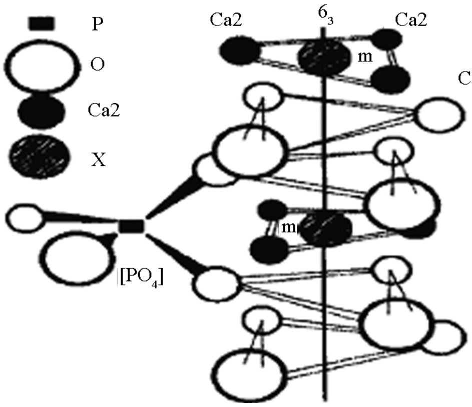


Fig. 6 The channel structure diagram of apatite[35]

Table 2 Some phosphate mineral solubility product

Mineral name	Chemical composition	$-pK_{sp}(lgK_{sp})$
Hydroxy pyromorphite	$Pb_5(PO_4)_3OH$	62.80
Chloro-pyromorphite	$Pb_5(PO_4)_3Cl$	84.43
$Cd_5(PO_4)_3OH$	$Cd_5(PO_4)_3OH$	56.49
$Cd_5(PO_4)_3Cl$	$Cd_5(PO_4)_3Cl$	49.66
$Zn_5(PO_4)_3OH$	$Zn_5(PO_4)_3OH$	49.10
$Zn_5(PO_4)_3Cl$	$Zn_5(PO_4)_3Cl$	37.53
$Cu_5(PO_4)_3OH$	$Cu_5(PO_4)_3OH$	51.62
$Cu_5(PO_4)_3Cl$	$Cu_5(PO_4)_3Cl$	53.96

Apatite can easily restrain heavy metals in its lattice by adsorption, ion exchange, co-precipitation and dissolution-precipitation.

4.2 Application of apatite family self-purification system

Apatite has good restraining and stabilizing ability to heavy metals, hence it can be widely applied in immobilizing toxic and harmful heavy metals in soil, sediment, tail-mine and water body. By adding apatite or soluble phosphate in hazardous pollutant system, inducing it to form low soluble apatite family minerals, the self-purification of various hazardous contaminants can be realized.

The stabilization of Pb^{2+} by apatite lies in dissolution-precipitation, that's to say, apatite dissolves, releasing $[PO_4]$, then, Pb^{2+} binds with PO_4^{3-}, forming precipitation of apatite family mineral pyromorphite. The adsorption and ion-exchange of Zn^{2+} and Cd^{2+} on the surface of apatite, and Ca-Cd/Zn hydroxyapatite co-precipitation may be the main mechanisms of apatite for immobilizing the two kinds of ions.

Pyromorphite, as the main weathering product containing Pb in soil, has common crystal structure with apatite, with low solubility, low leaching ratio, high pH stability, etc.

Zhang et al. used hydroxyapatite to immobilize and stabilize the sulfides of Pb in various pH conditions, pointing out that Pb can completely transformed into pyromorphite in half an hour in acid condition[36]. Zhang et al. used different phosphate to immobilize and stabilize Pb in soil, finding when adding soluble phosphate, the product pyromorphite formed promptly; when adding hydroxyapatite, the forming speed of pyromorphite decreased markedly[37]. Scheckel et al. used the method of forming pyromorphite in situ with phosphate treating soil polluted by chloride of lead, pointing out over 90 % of Pb transformed into pyromorphite in the beginning 30 seconds of reaction, and the immobilization ratio of Pb arrived at 93 % ~100 % in six hours[38]. The research of Ruby et al. also demonstrated that phosphate can reduce the leaching toxicity, immobility and biological activity of Pb in polluted soil[39]. Theodoratos et al. treated soil polluted by heavy metals using soluble phosphate, concluding that heavy metals Pb and Cd are well immobilized, but only little As and Zn are immobilized[40]. Raicevic et al. used hydroxyapatite to immobilize the heavy metals in polluted soil, finding that apatite can effectively reduce the exchangeable Zn, Pb, Cu and Cd in soil[41].

The immobilization of MSW fly ash using phosphate is an orientation paid more attentions. Eighmy et al. treated fly ash using soluble phosphate, demonstrating that the restrain of phosphate to heavy metal ions by precipitation is stronger than adsorption on surface of phosphate[42]. Jiang et al. immobilized the fly ash using soluble phosphate and apatite, and proposed that phosphate has good stabilization effect on fly ash[43]. When 3 % soluble phosphate was added, the leaching concentration of heavy metals Pb, Cd and Zn in fly ash decreases 97.15 %, 91.16 % and 95.15 %, respectively; moreover, the fly ash sample, after immobilization, stabilized in a quite wide pH range.

5 Prospect for self-purification system application for heavy metal pollutants

The naturally occurring minerals, containing heavy metals and stably existing in nature, provide us with theoretical base for designing and constructing hazardous pollutant self-purification system. Treating potential environment issues using the natural self-purification function of minerals has virtues of low cost, good immobilization effectiveness on heavy metals, simple technology, and no secondary pollution etc. By researching the self-forming principle of soil minerals combined with the chemical composition characteristics of hazardous pollutants that needed for purification and remediation, simulating the forming condition of certain mineral in nature, it can be realized that inducing and controlling the toxic and harmful compositions reacting with other industrial contaminants and then self-forming can attain clay-like minerals. These clay-like minerals can be attempted to be used for safe disposal of hazardous material landfill, sludge, sediment, and metal tail-mine by immobilization in situ; self-purification treatment and disposal of electroplating and dying waste water; stabilization and remediation of soil polluted by heavy metals in situ; hazardous material pollution control and new barrier system of Permeable Reactive Barrier and so on that prevent contaminants from migrating into underground water.

The key issue for designing self-purification system of heavy metal-bearing hazardous wastes is to find and design the minerals with self-purification effectiveness on the pollutants, aiming at the characteristics of heavy metal-bearing contaminants according to geognosy theory. Meanwhile, based on the physical-chemical principle of minerals, it is also necessary to induce the self-forming of expected minerals in contaminants-bearing self-purification system. Hence, several problems below need to be resolved:

1) The chemistry of clay-like mineral phase used for pollution control by immobilizing the contaminants, the equilibrium relationship of coexisted mineral phases, the thermodynamics and kinetics of self-forming reactions;

2) The cations/anions exchange capacity of self-forming clay-like minerals and distributing correlation;

3) The chemistry and mechanism of surface adsorption of heavy metals on clay-like minerals;

4) The adsorption and distribution effect of contaminants in self-forming layer clay minerals;

5) The chemical stability of heavy metal in clay mineral structure in multimedia environment.

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