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Reliable Mine Water Operations

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Treatment on U and Mn in Drainage of a Uranium Mill Tailing Pond

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Abstract Waste water of a uranium mill tailing pond and its composition are investigated with pH, U, Ra, Mn, F. Based on the investigation, a kind of method is selected through experiments, and the drainage is neutralized by lime milk first, and adsorbed by pyrolusite so as to make U, Ra, Mn and pH meeting the requirements of emission control regulations.

Keywords waste water treatment, uranium mill, environment protection, tailings water management

Introduction

Low level radioactivity waste water from the uranium mill contains usually U, Th, Ra etc. radioactive elements and Mn, Hg, Cd etc. metal elements which badly influences environment. In order to prevent the pollution, relevant emission control regulations have been constituted by China government. Chemical precipitation, ion-exchange, evaporation, physical or chemical adsorption, membrane or microorganism treatment etc. are now used to reduce such water contamination degree.

A uranium mill in south China processes uranium ores by acid-stirring-leaching progress for yellowcake. The leached tailing is moved into a special tailing pond which has already stored millions tons of tailing. The tailing pond releases 40…100 m^3/h waste water which contains some radioactive items and other pollutants. Therefore necessary treatment on this drainage is required to protect local environment.

Methods

Waste water samples were taken from the main outlet of the pond so as to have good representativeness. Chemical compositions are listed in Table 1.

According to local environment demand, water discharged into environment should comply with the second grade of the integrated waste water discharge standard (GB 8978–1996). Also according to regulation for the radiation protection of uranium mine and mill (EJ993-2008), the allowed uranium concentration is 0.3 mg/L, 1.1 Bq/L as ^{226}Ra. The highest Mn^{2+} concentration is 2.0 mg/L, F^- 10 mg/L and pH from 6 to 9. The results in Table 1 show that the main contaminants of this pond water are U, Mn^{2+}, ^{226}Ra, F^- and pH.

Low valence sulfur in uranium mine's tailing is oxidized by O_2 in air or other natural oxidants and becomes sulfuric acid which causes water pH below the lower limits of the discharge regulations. Also remained sulfuric acid from extraction progress induces pH pollution. Uranium contaminant comes from uranium ores which is not extracted from leaching process but later released gradually. The free uranium sulphate remained in fis-

U	Mn	^{226}Ra ①	pH	SO_4^{2-}	∑Fe	Ca	Mg	Al	Cl^-	F^-	P	H_2SO_4	As	Hg	SiO_2
1.5	26	5.1	4.5	1300	<1	373	81	26	477	22.6	<1	179	<0.005	<0.0005	24

Note①: ^{226}Ra unit Bq/L

Table 1 *Chemical composition mg/L*

Waste water volume /mL	CaO weight /g	pH value	ρ(U)/(mg•L^{-1})	ρ(Mn^{2+})/(mg•L^{-1})
500	0.06	7.20	0.05	23
500	0.08	7.75	0.08	21
500	0.09	8.41	0.11	18
500	0.10	8.61	<0.05	15

***Table 2** Relationship between CaO weight, pH and remained uranium concentration*

sures of leached ores also cause uranium pollution when it moves from ores to water, so as the Ra pollution. Mn^{2+} comes mostly from manganese dioxide used as oxidant in leaching process and some is extraction production in uranium ores leached by sulfuric acid.

Under acidic condition Mn^{2+} is stable and hard to remove. Generally treating Mn^{2+} pollution needs adding alkali to make water neutral or alkaline thus Mn^{2+} can be easily transferred to Mn^{4+} and precipitates as pyrolusite. F^- can also be removed during precipitation process. Flocculating settling of Mn^{2+} with lime slurry can accelerate metal precipitation. Mn^{2+} can be adsorbed by pyrolusite under neutral or alkaline condition. The main reactant in pyrolusite bed is actually manganese dioxide. Mn^{2+} is transferred to solid manganese dioxide and pyrolusite can eternally be refreshed theoretically. Meanwhile the precipitation gel can also assist adsorption of other water pollutants, such as Ra. In general the treating plan for this pond water is: neutralized by milk of lame and precipitation, oxidized and adsorbed by pyrolusite bed.

CaO and $KMnO_4$ for experiments are analytic reagents. Precipitation and oxidation experiments proceed in appropriate beakers. Pyrolusite adsorption experiments are carried on in a glass column which is 350 mm high and 25 mm diametrical. The pyrolusite sand particle size ranges from 1-2 mm, 2-4 mm to 4-8 mm. The coarser sand is placed on the bottom of the column and the fine one on the top. From top to bottom, sand bed height is 103 mm, 96 mm, 116 mm and sand weight is 81.5 g, 80.0 g, 86.7 g in turn.

Adjusting pH and removing U, F^-

Solution pH value can be adjusted to normal level by adding CaO. Meanwhile small quantity of uranium in water can also be removed through precipitation. Relationship between CaO weight, pH and remained uranium concentration is shown in Table 2.

Experiment results indicate that adding 0.12 g CaO into one liter waste water makes pH reach acceptance value and uranium can be removed mostly at the same time. The more CaO is added, the less Mn^{2+} is remained. To reduce Mn^{2+} for further treatment convenience and make sure that pH and U emission lower than regulations limits final pH value is settled as 8.6. Under this condition CaO will be added as 0.2 g per liter water. At this point remained F^- is about 10 mg/L which meets the requirement of emission control regulations and remained Ra is about 2.0 Bq/L which is just a little higher than the limits. Further Ra treatment is necessary.

Removing Mn^{2+}, Ra

After adjusting pH and removing U, F^- process, the treated water sample is used for further removing Mn^{2+}, Ra experiments.

Removing Mn^{2+} through oxidation

Mn^{2+} can be quickly oxidized by proper quantities of potassium permanganate and no new contaminant will be introduced. Adding potassium permanganate experiment results are shown in Table 3.

Mn^{2+} in waste water can be oxidized by potassium permanganate effectively. The efficiency of removing Mn^{2+} is high enough when

Waste water volume /mL	Potassium permanganate weight /g	Filtrate color	ρ(Mn^{2+}) /(mg•L^{-1})	Eh /mV
400	0.01	mauve	-	622
425	0.01	pink	<1.0	619
450	0.01	colorless	<1.0	614
475	0.01	colorless	<1.0	606
500	0.01	colorless	6.0	581

Table 3 *Adding potassium permanganate experiment results*

system Eh is about 606 mV meanwhile Mn^{2+} concentration is less than 1 mg/L that is lower than regulation limits. The dosage is 21 g KMnO$_4$ per ton waste water, a little bit more than the theoretical demand.

Mn^{2+} adsorption by pyrolusite sand

Factors such as dissolved oxygen consistency, flowrate (contacting time) and activation time can influence absorption efficiency of Mn^{2+} by pyrolusite sand. Aeration can accelerate oxygen dissolubility and the experiments can tell whether it will be helpful for Mn^{2+} adsorption. Different aeration time is applied while aeration intensity is settled as 3.2 L/min (air). After aeration the solution flows immediately from top to bottom passing the sand bed at a flowrate of 10 mL/min. Results shown in Table 4 indicate that aeration has little affection on Mn^{2+} adsorption by pysolusite sand.

When waste water flows through the sand bed once at 5 mL/min Mn^{2+} can be adsorbed effectively as shown in table 5. This single-stage treatment efficiency is not very stable probably because the manganese dioxide sand bed is still under activation.

Multi-stage treatment experiments are conducted as the single-stage treatment efficiency is not stable (from 40 % to 60 %). 3.0 L waste water flows through the pyrolusite sand repeatedly and at the end of each circulation some water samples are taken and analyzed for Mn^{2+}. The Mn^{2+} concentration is shown in Fig. 1. Two times circulation later Mn^{2+} concentration decrease to less than 1mg/L and after some more times circulation Mn^{2+} concentration maintains low level below the emission control limits. Mn adheres to the sand steadily and does not dissolve back into water again.

20 L waste water has flowed through the manganese sand bed at 5 mL/min since experiments started. About 300 mg Mn^{2+} has been adsorbed by 248.2 g the sand bed. Mn^{2+} adsorption is not saturated yet when the experiment finished. The sand bed is still stable and intact. There is no obvious decline for waste water traffic ability. After this treatment re-

Aeration time /min	ρ(Mn^{2+})/(mg•L^{-1})
0	15
20	16
40	17
60	15

Table 4 *Adsorption results of different aeration time*

Waste water volume /mL	ρ(Mn^{2+})/(mg•L^{-1})	Removing efficiency/ %
420	6.0	60.0
840	7.0	53.3
1260	6.0	60.0
1680	7.0	53.3
2100	8.0	46.7
2520	9.0	40.0

Table 5 *Mn^{2+} adsorption by manganese sand*

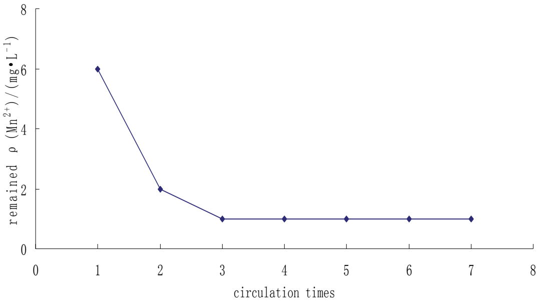

Figure 1 *Mn^{2+} concentration after repeated adsorption by sand*

mained Mn^{2+} concentration keeps lower than the emission control limits.

Removing Ra

Generally Ra is removed with precipitation by adding $BaCl_2$ then neutralized with milk of lime slurry. It also can be adsorbed by manganese dioxide sand when Mn^{2+} is oxidized into $Mn(OH)_2{\cdot}nH_2O$, some kind of gel who has large specific surface area which makes pyrolusite sand has extra adsorption ability.

Activity degree of ^{226}Ra is analyzed after series experiments mentioned above. After adjusting pH and removing U, F^- process, the remained ^{226}Ra activity degree has decreased from 5.07 Bq/L to 2.0 Bq/L, which is a little higher than regulations limits. After adding potassium permanganate the value is 1.0Bq/L and after pyrolusite sand adsorption experiments it is 0.0933 Bq/L. On two conditions remained ^{226}Ra activity degrees are both less than the emission limit 1.1 Bq/L.

Conclusions

Main contaminants of this tailing pond drainage are U, Ra, Mn^{2+}, F^- and pH. U concentration is 1.54 mg/L, ^{226}Ra activity degree is 5.07 Bq/L, Mn^{2+} concentration is 26 mg/L, F^- 22.6 mg/L, and pH value is 4.5. On the first we add CaO into waste water, adjust pH to 8.6, remove U, F^- through precipitation. At the same time, pH value meets the demand of the integrated waste water discharge standard. Mn^{2+} is partially removed with precipitation after filtration. Add KMnO4 into filtrate, or use pyrolusite sand to oxidize Mn^{2+} in the filtrate. Both methods can make Mn^{2+} concentration lower than emission control limit 2.0 mg/L. All these treatment steps make sure that the waste water contaminants can be removed and treated water is eligible to discharge. Manganese sand adsorption is cheap and easily executed, so this method is preferable compared with oxidation method by potassium permanganate.

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