含铀硼镁铁矿硫酸浸出液除铀的研究 *

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摘要　辽宁省翁泉沟含铀硼镁铁矿的硫酸浸出液主要成分是 H_3BO_3 和 $MgSO_4$，并含有少量 Fe^{3+}（Fe^{2+} 已用 $NaClO_3$ 氧化为 Fe^{3+}）和 UO_2^{2+}. 本研究用 MgO 调节溶液的 pH 值，进行了含铁与不含铁 2 种溶液的除铀试验. 当溶液不含 Fe^{3+} 时，靠 UO_2^{2+} 自身沉淀后，溶液中 U 浓度高于硫酸浸出液中的 U 含量，无法将铀除去. 而利用酸浸液中的 $Fe(OH)_3$ 作共沉淀剂，可以降低其中的 U 含量，并且随着初始酸浸液中 U 含量的降低，而净化液中的 U 含量也随之降低. $Fe(OH)_3$ 吸附载带铀的最佳 pH 值为 5.8 左右.

关键词　U，$Fe(OH)_3$，共沉淀，除铀.

　　$Fe(OH)_3$ 吸附铀与溶液的 pH 值、溶液的组成以及铀、铁含量等因素有关. 在约中性的溶液中 $Fe(OH)_3$ 对铀有最大的吸附率[1]，当溶液中含有 CO_3^{2-} 时，可与 UO_2^{2+} 离子形成稳定的 $UO_2(CO_3)_2^{2-}$ 及 $UO_2(CO_3)_3^{4-}$ 络合物，影响铀在 $Fe(OH)_3$ 上的吸附[2]. Van der Weijden[3]，Hsi Ching Kuo Daniel[4]，Anand Ram Gupta[5] 等都曾对一些无机物吸附铀的机理进行过探讨.

　　本试验用硫酸分解辽宁省翁泉沟含铀硼镁铁矿，用 MgO 调节酸浸液 pH 值，以达到除去铁和铀的目的.

1　实验方法

　　试验溶液是辽宁省翁泉沟含铀硼镁铁矿的硫酸浸出液，用分析纯试剂配成. 实验在带搅拌器及冷凝器的三口瓶中进行，用电热套加热，温度控制在 95℃. 取 100 ml 预先配好的试液装入三口瓶内，开动搅拌器及加热套，温度升至 95℃后，加入轻质氧化镁，调节溶液的 pH 值. 加入氧化镁后开始计时. 预实验表明，搅拌 1 h 与 3 h $Fe(OH)_3$ 对铀的吸附沉淀率变化不大，故实验操作均 1 h. 停止搅拌后，将试验体系恒温静置，待固相沉淀以后，取上层清液过滤，滤液的分析测定均在常温下进行.

　　实验中用 pHS-2 型酸度计测定溶液的 pH 值；Mg^{2+} 用 EDTA 络合滴定法测定；SO_4^{2-} 的分析用重量法；H_3BO_3 的分析以甘露醇作络合剂，用 NaOH 滴淀；U 含量以偶氮胂 Ⅲ 作显色剂，用分光光度法测定.

2　实验结果及讨论

2.1　不含铁时酸浸液沉淀铀的试验

　　试液组成见表 1.

表 1　配制试液的组成（不含铁）[1]

组成	SO_4^{2-}	Mg^{2+}	H_3BO_3	UO_2^{2+}	NO_3^-
含量 /mol·L^{-1}	1.4276	1.3969	0.6053	0.01733	0.03466

1) pH 值约为 1（计算值）

　　UO_2^{2+} 在含有大量 SO_4^{2-} 的溶液中，除了随着 pH 值改变发生水解反应[6]生成羟基铀酰络阳离子外，还与溶液中的 SO_4^{2-} 发生络合反应[7,8]，生成硫酸铀酰络合离子. 其反应式：

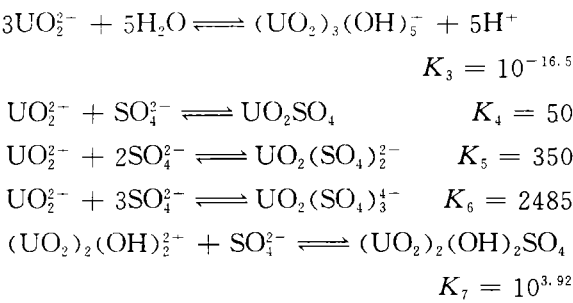$$UO_2^{2+} + H_2O \rightleftharpoons UO_2(OH)^+ + H^+$$

$$K_1 = 10^{-5.7}$$

$$2UO_2^{2+} + 2H_2O \rightleftharpoons (UO_2)_2(OH)_2^{2+} + 2H^+$$

$$K_2 = 10^{-5.92}$$

$$3UO_2^{2+} + 5H_2O \rightleftharpoons (UO_2)_3(OH)_5^- + 5H^+$$
$$K_3 = 10^{-16.5}$$
$$UO_2^{2+} + SO_4^{2-} \rightleftharpoons UO_2SO_4 \qquad K_4 = 50$$
$$UO_2^{2+} + 2SO_4^{2-} \rightleftharpoons UO_2(SO_4)_2^{2-} \qquad K_5 = 350$$
$$UO_2^{2+} + 3SO_4^{2-} \rightleftharpoons UO_2(SO_4)_3^{4-} \qquad K_6 = 2485$$
$$(UO_2)_2(OH)_2^{2+} + SO_4^{2-} \rightleftharpoons (UO_2)_2(OH)_2SO_4$$
$$K_7 = 10^{3.92}$$
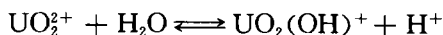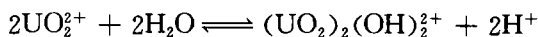
K_1、K_2、K_3 为常温下 UO_2^{2+} 的水解常数，K_4、K_5、K_6、K_7 为 25℃ 时 UO_2^{2+} 与 SO_4^{2-} 的络合稳定常数.

用氧化镁调节酸浸液的 pH 值，在铀未沉淀之前，通过以上 8 个反应，可以近似计算出不同 pH 值铀在溶液中的存在形态，见图 1. 它表明溶液中 UO_2^{2+} 在 pH 值小于 7 时主要以 $UO_2(SO_4)_2^{2-}$、$UO_2(SO_4)_3^{4-}$、$(UO_2)_2(OH)_2SO_4$ 形式存在，当 pH 值高于 7 时 UO_2^{2+} 的水解络合物 $(UO_2)_3(OH)_5^-$ 比例就明显升高，成为 UO_2^{2+} 的主要存在形态.
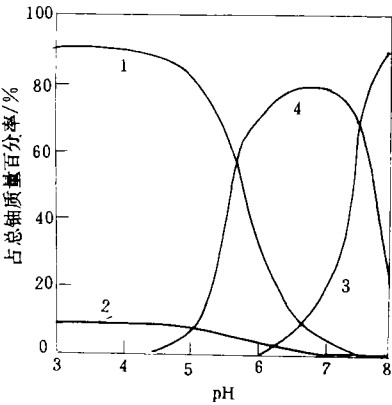
图 1　pH 值对溶液中铀存在形态的影响
1. $UO_2(SO_4)_3^{4-}$　2. $UO_2(SO_4)_2^{2-}$
3. $(UO_2)_3(OH)_5^-$　4. $(UO_2)_2(OH)_2SO_4$

图 2 是用氧化镁调节硫酸浸出液的实验结果. 从图 2 可以看出，随着 pH 值升高，净化液中铀的总含量逐渐降低，其变化趋势与文献[6]值相似，在 pH 值小于 6.13 的范围之内铀含量单调地下降.

2.2　含铁时酸浸液沉淀铀的试验
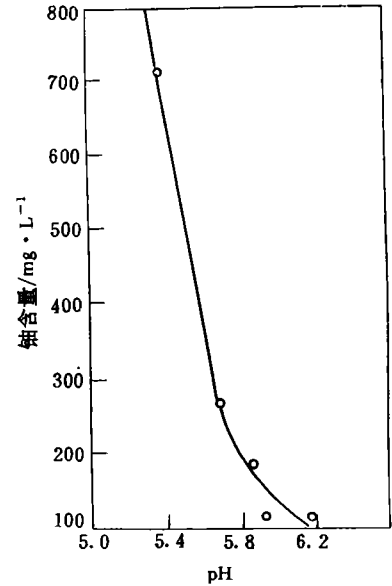
用 2 种不同铀含量溶液进行试验. 其试液组成见表 2. 2 者铀的浓度相差 10 倍，其它组分的浓度相同.

图 2　pH 值与溶液中铀含量的关系

表 2　硫酸浸出液试液的组成[1] /mol·L^{-1}

溶液	SO_4^{2-}	Mg^{2+}	H_3BO_3	Fe^{3+}	NO_3^-	UO_2^{2+}
I	1.4154	1.3152	0.5528	0.03457	2.258×10^{-4}	1.129×10^{-4}
II	1.4154	1.3152	0.5528	0.03457	2.356×10^{-3}	1.178×10^{-3}

1) pH 值约为 1(计算值)

经加入氧化镁沉淀铁、铀后，溶液中的硼含量都没有多大的变化，故 $Fe(OH)_3$ 沉淀对硼的吸附是很弱的，可以忽略. 此外 pH 值大于 5 以后，溶液中 Fe^{3+} 均已完全沉淀. 表 3 是不同 pH 值条件下沉淀铀的实验结果.

图 3、图 4 分别表示溶液 I、溶液 II 净化液中铀浓度与 pH 值的关系，比较图 3 与图 2 可知，溶液 I 的铀含量虽未经净化已经低于不含铁经自身沉淀后溶液的铀含量，可见溶液 I 沉淀的铀主要是靠 $Fe(OH)_3$ 吸附载带而沉淀的. 溶液 II 铀含量虽高，但经净化后溶液中的含量，也不同程度比相同 pH 值情况下不含铁溶液中的铀含量低，说明溶液 II 沉降的铀除靠铀自身沉淀外，还有靠 $Fe(OH)_3$ 吸附载带的.

铀、铁共沉淀过程中，溶液的 pH 值明显影响铀的沉淀率，铀与 $Fe(OH)_3$ 共沉淀的最佳 pH 值为 5.8 左右.

表3　硫酸浸出液试液净化铀实验结果

| 溶液	浸出液 U 含量 $\times 10^4$/mol·L^{-1}	净化液 U 含量 $\times 10^5$/mol·L^{-1}	U 的沉淀率/%	净化液 pH 值
溶液 I	1.129	9.979	11.61	3.11
	1.129	4.286	62.04	5.08
	1.129	3.361	70.23	5.51
	1.129	1.849	83.62	5.60
	1.129	1.912	83.06	5.72
	1.129	2.374	78.97	6.06
	1.129	2.563	77.30	6.36
	1.129	2.718	75.93	6.43
	1.129	3.403	69.86	6.54
	1.129	4.622	59.06	6.87
	1.129	5.252	53.48	7.34
溶液 II	11.78	42.86	63.62	5.14
	11.78	29.15	75.25	5.37
	11.78	28.47	75.83	5.56
	11.78	15.17	87.12	5.62
	11.78	18.49	84.30	5.72
	11.78	32.56	72.36	5.96
	11.78	45.17	61.66	6.28
	11.78	51.16	56.57	6.60
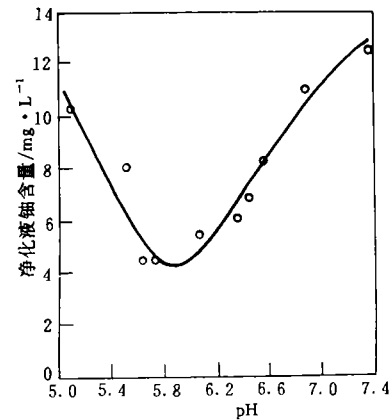
图3　pH 值与溶液 I 净化液中铀含量的关系

根据 Upor[2]，Hsi Ching Kuo Doniel[4]碳酸铀酰络合离子不能被 Fe(OH)$_3$ 吸附，因而推断硫酸铀酰离子也不易被 Fe(OH)$_3$ 吸附. 当溶液中的 UO_2^{2+}、$UO_2(OH)^+$、$(UO_2)_2(OH)_2^+$、$(UO_2)_3(OH)_5^+$ 等离子被 Fe(OH)$_3$ 吸附沉淀后，将促使硫酸铀酰的络合物电离，产生可供吸附的离子. Старик[9]在研究 Fe(OH)$_3$ 胶体吸附铀时发现，Fe(OH)$_3$ 胶体的电性随溶液的 pH 值而变化. 笔者认为 Fe(OH)$_3$ 表面的正电对 UO_2^{2+} 及带正电的水解产物有一定的排斥作用，使得低 pH 值条件下铀的吸附率不高，随着

Fe(OH)$_3$ 表面电性的转变，铀的吸附率增加，但是 pH 值的增加，UO_2^{2+} 将进一步水解形成中性物质和胶体粒子，降低了带正电荷的 UO_2^{2+} 及水解阳离子的比例，使得吸附减少，这2种因素共同作用的结果，出现了中性溶液附近铀沉淀率的最大值.
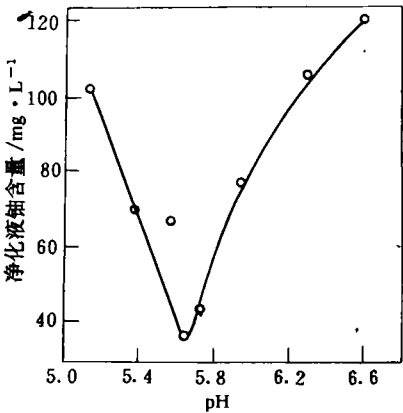

图4　pH 值与溶液 II 净化液中铀含量的关系

3　小结

（1）本实验结果证明 Fe(OH)$_3$ 对铀的吸附载带，在铀沉淀过程中起着重要的作用.

（2）在硫酸盐体系中，Fe(OH)$_3$ 胶体吸附载带铀的最佳 pH 值为 5.8 左右.

（3）对不同 U 含量浸出液净化发现，如果硫酸浸出液中 U 含量降低，则净化液中 U 浓度也随之降低. 如果利用硫酸浸出液本身的含铁量，净化液中的 U 含量可以从 24 mg/L 降到 4.5 mg/L 左右.

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et al. (Dept. of Environ. Eng. , Tsinghua U-niv. , Beijing 100084): *Chin. J. Environ. Sci.* , **17**(4), 1996, pp. 14—17

Two catalysts were prepared and used for pre-treatment of typical dye intermediate wastewater —— tobias acid wastewater by metal oxide cat-alyzed ozonation. For wastewater with initial COD concentration of 1500 mg/L, when ozona-tion dose is 0. 82 g/L, COD removal efficiency is above 50%. And Ozonation Index (OI) of the two catalysts are 1. 44 and 0. 7 respectively, while the blank γ-Al_2O_3 is 1. 90. The ozonation products of tobias acid identified by gas chro-matography-mass spectrography are o-benzendi-carboxylic acid, oxalic acid, sulphate ion and ni-trate ion, and then the ozonation pathway is pro-posed. After tobias acid is treated by metal oxide catalyzed ozonation, the biodegradability is im-proved apparently.

Key words: tobias acid wastewater, catalyst, metal oxide catalyzed ozonation.

Removal of 9 Kinds of Trace Element in Bur-ning Coal in the Layer-Burning Boilers. Wang Qichao et al. (Changchun Institute of Geogra-phy, Chinese Academy of Sciences, Changchun 130021), Wang Zhigang et al. (Environmental protection Institute of Northeast Coal Industry): *Chin. J. Environ, Sci.* , **17**(4), 1996, pp. 18—20

An empirical formula on the content of trace ele-ments as Be, Co, Cr, Cu, Mn, Ni, Pb, V, Zr in fly ash and bottom ash of burning coal in layer-burning boilers was developed, by which the dis-tribution and transfer quantity of trace elements from coal into fly ash, bottom ash and atmo-sphere was calculated. The grain size distribution of content and mass of trace elements in fly ashes was also studied, and the laws of enrichment or dispersion of trace elements in burning process were approached. The content of most of trace elements in bottom ashes is higher than that in fly ashes, most quantity of 9 trace elements in coal is removed into bottom ash after burning, but the enrichment factor of element in fly ashes is higher than that in bottom ashes. The enrichment ex-tent of trace elements in fly ashes increases as grain size decreases. About 90 percent of total quantity of trace elements in fly ashes are dis-tributed in the particles with the diameter less than 0. 125 mm.

Key words: layer-burning boiler, burning coal,

trace element, removal.

The Application of Surfactants on Treatment of Petroleum-contaminated in Unsaturated Zone. Zhu Mei and Xu Jialin (Institute of Environ. Sci. , Beijing Normal University, Beijing 100875), Tian Honghai (Center of Environ. Sci. , Peking University, Beijing 100871): *Chin. J. Environ. Sci.* , **17**(4), 1996, pp. 21—24

The paper focused on the application of aqueous surfactant washing for cleaning up petroleum con-tamination in unsaturated zone. Regional geo-graphical features and contamination characteris-tics have been investigated. Nine commercial non-ionic surfactants were analyzed and tested. Their critical micelle concentrations were measured and their effects on emulsification and solubilization of oil and benzene as well as on soil dispersion were compared. The results showed that the best sur-factants are AEO-9 and SA-20, i. e. , alcohol polyethoxylated ethers. Their optimum concen-trations were also determimed. In batch-washing tests the highest removal efficiency can be as high as 94%. Results of leaching tests for soil columns and lime stone columns were satisfactory as well. From this study, it is clear that the application of surfactants can be included in field experimental research for the treatment of contaminated unsat-urated zone of groundwater.

Key words: groundwater, petroleum contamina-tion, surfactant, unsaturated zone.

Studies on Removing Uranium from Digested So-lutions of Uranium Bearing Ascharite-Magnetite Syngenetic Mineral by Sulfuric Acid in Wengquegou Liaoning Province. Cao Jiling et al. (School of Chemical Engineering, Dalian Univer-sity of Technology, Dalian 116012): *Chin. J. Environ. Sci.* , **17**(4), 1966, pp. 25—27

The digested solution of uranium bearing as-charite-magnetite syngenetic mineral in Wengque-gou by sulfuric acid contains a large amount of H_3BO_3 and $MgSO_4$ and a little Fe^{3+} (after oxida-tion with $NaClO_3$)and UO_2^{2+}. The experiments of removing uranium from solutions containing Fe^{3+} and without Fe^{3+}, after adjusting their pH with MgO, were carried out. After precipitation of UO_2^{2+} from solution without Fe^{3+}, the U content is still higher than that in digested solution, whereby it is impossible to remove U. When $Fe(OH)_3$ exists, which can act as coprecipitant, the U content after purification can be depressed,

the U content after purification decreases with decrease of U content in digested solution. The optimum pH for coprecipitation is about 5. 8.

Key words: U, Fe(OH)$_3$, coprecipitation, removing uranium.

Study on Correlation Between Influent and Effluent Substrate Concentrations of Biofilm Reactor.

Yu Liu(Dept. of Civil and Structural Eng. , Hong Kong Univ. of Science and Technology, Hong Kong), Qingliang Zhao (Dept. of Environ. Eng. , Harbin Univ. of Architecture and Eng. , Harbin 150001): *Chin. J. Environ. Sci.* , **17**(4), 1996, pp. 28—30

This paper mainly investigated the effect of influent substrate concentration(S_0)on steady state effluent quality (S_e) for anaerobic, heterotrophic-aerobic and nitrifying biofilm reactors. It was found that variation pattern of S_e as S_0 changes is subject to a semi-U shaped curve. Based on the known linear model, a nonlinear S_0-S_e model was developed. It was demonstrated that this model can provide a quantitative description for experimental data, also was confirmed by the data from literature. The proposed concept of critical influent substrate concentration has great importance in future design and operation of biofilm reactor.

Key words: biofilm, substrate, reactor, modeling.

Automatic Control of Polymer Addition for Belt Press Sludge Dewatering System.

Tian Xiumin et al. (Research Institute of Machinery Seience and Technology, Beijing 100044): *Chin. J. Environ. Sci*, **17**(4), 1996, pp. 31—32

The relation between polymer dosage and sludge concentration had been determined. The model of automatic control for polymer addition was established. The control system was installed on a two-metre belt press dewatering raw sludge of Tangshan Xijiao Sewage Treatment Plant by measuring sludge concentration and flow rate in line. The evaluation was conducted by comparing the results of historical manual operation with those achieved on the same press under automatic control. Analysis of the data indicated that average 15% polymer can be saved, the dewatering effect can be improved and more uniform performance of the dewatering machine will be realized.

Key words: sludge dewatering, belt press, automatic control for dosage.

Photocatalytic Degradation of Organophosphorus Pesticides Using TiO$_2$ Supported on Fiberglass.

Chen Shifu et al. (Dept. of Chem. Eng. , Zhengzhou Institute of Technology, Zhengzhou 450002): *Chin. J. Environ, Sci.* **17**(4), 1996, pp. 33—35

Photocatalytic degradation of organophosphorus pesticides using supported TiO$_2$ as a catalyst, which is prepared by thermal decomposition and calcination of colloidal solution made from hydrolytic of titanium tetraisopropoxide [Ti(iso-OC$_3$H$_7$)$_4$]on fiberglass was studied. The results showed that four organophosphorus pesticides of lower concentrations were completely photocatalytically degraded into PO$_4^{3-}$ within a short time illumination with a medium pressure mercury lamp of 375 W. The TiO$_2$ supported on the fiberglass was not removed easily, after 120 h illumination there was no significant loss of the photocatalytic activity of TiO$_2$, it could be used continually. The reasons of the different chemical structures of organophosphorus pesticides affecting photodegradation efficiency were investigated.

Key words: supported TiO$_2$, photocatalytic degradation, organophosphorus pesticides, titanium tetraisopropoxide.

Ecological Effects of Multi-Effects-Triazole on Soil Microbe.

Gong Ping (Institute of Applied Ecology, Chinese Academy of Sciences, Shenyang 110015), G. Beudert (Institute for Aquatic Environmental Engineering, University of Karlsruhe, D-76128 Karlsruhe, F. R. Germany): *Chin. J. Environ. Sci.* , **17**(4), 1996, pp. 36—38

Effects of multi-effects-triazole(MET)on soil nitrification, dehydrogenase activity(DHA), respiration and microbial biomass C were investigated through laboratory incubation and field experiments. It is derived from this study that MET has no adverse long-term influence on soil microbe. However, its short-term effects are notable and need further studies.

Key words: multi-effects-triazole (MET), soil microorganism, ecological effects.

An Interaction between *Scenedesmus obliquus* and N-(2, 4-dimethylphenyl)-N'-methylformamidine.

Yan Hai et al. (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085): *Chin. J. Environ.*