

链层状矿物—坡缕石的酸溶解、吸附和解吸附的表面矿物学机理

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Surface-Mineralogical Mechanism of Acid Disolution, Adsorption, and Desorption for Chain-Layer Mineral: Palygorskite

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本论文在对苏皖地区两个凹凸棒粘土的系统的矿物学研究的基础上,选定安徽明光官山的粉红色和灰白色凹凸棒粘土进行了提出,得到了富镁和贫镁的两个坡缕石。对两个坡缕石同样进行了系统的矿物学研究,粉末XRD定性分析结果显示富镁者呈粉红色、为一正交晶系矿物,贫镁者呈灰白色、较单一的单斜晶系矿物;二者晶体结构中Mg/(Fe<sup>3++</sup>Al<sup>3+</sup>)比值分别为3.8(粉红色)和1.4(灰白色者)。经FTIR和NIR反射光谱的研究,确认富镁坡缕石为一三八面体矿物,而贫镁者为介于二八面体和三八面体之间的矿物。对富镁和贫镁坡缕石进行了系统的酸浸蚀实验,实验结果显示两个坡缕石的四面体离子(Si<sup>4+</sup>)在浸蚀过程中具有相同的溶出规律,而八面体离子的溶出规律却具有较大差异。在3和5mol/L的盐酸溶液中,Si<sup>4+</sup>的浸出呈三阶段特征;而在1mol/L盐酸溶液中,Si<sup>4+</sup>的浓度随酸浸蚀时间的延长而增大。对灰白色坡缕石而言,所有浓度的盐酸对八面体离子的浸出浓度均随浸蚀时间的延长而增大。而对粉红色坡缕石而言,在1mol/L的盐酸溶液中,浸出的八面体离子的浓度随酸浸蚀时间延长而增大;但在3和5mol/L的盐酸溶液中,浸出八面体离子的浓度随时间的延长表现出三阶段特征。导致Si<sup>4+</sup>和粉红色坡缕石的八面体离子在3和5mol/L的盐酸溶液中呈三阶段特征的原因可能来自Si<sup>4+</sup>和Mg<sup>2+</sup>溶出行为的相互制约。两个坡缕石的Mg/(Fe<sup>3++</sup>Al<sup>3+</sup>)比值随盐酸浸蚀时间的延长逐渐趋向一个定值。在1mol/L盐酸中Mg/(Fe<sup>3++</sup>Al<sup>3+</sup>)比值是随浸蚀时间延长逐渐增大并稳定在2.0左右(贫镁坡缕石)和4.0左右(富镁坡缕石),而3和5mol/L盐酸中Mg/(Fe<sup>3++</sup>Al<sup>3+</sup>)比值在短时间内内增大到极大值,然后逐渐减小并稳定在2.0和4.0左右。在酸浸蚀的开始阶段,阳离子的溶出主要通过晶体表面的扩散作用来进行,此时,裸露表面几层的原子和离子不仅有八面体离子,而且有四面体离子,其中部分四面体为Al<sup>3+</sup>占位,因此Mg<sup>2+</sup>/(Fe<sup>3++</sup>Al<sup>3+</sup>)的比值偏低。随着浸蚀作用的进行,化学反应逐渐成为主导因素,对Mg<sup>2+</sup>的选择性优先溶出导致Mg<sup>2+</sup>的溶出量逐渐增大,而且HCl溶液对坡缕石的结构微空腔的渗透,从而使HCl溶液对坡缕石的浸蚀是全面的,酸中的Mg<sup>2+</sup>/(Fe<sup>3++</sup>Al<sup>3+</sup>)稳定在一个定值上。总之,坡缕石在酸中活化过程受两种机制控制:扩散机制和化学反应机制。对酸浸蚀残留物的粉末XRD研究显示:少于7小时盐酸浸蚀时,固体残留物依然是坡缕石;360小时酸浸蚀坡缕石残留物的XRD图谱上行射线出现明显的宽化,且在衍射线均出现不同程度的分裂现象,在20~30°范围内形成一宽大的包络峰,表明360小时浸蚀后残留物已经不是坡缕石。据AFM和TEM镜下的残留物的微形貌观察知随酸浸蚀时间的延长,残留物中微小的球状颗粒明显增多。360小时的酸浸蚀后残留物中出现大量的微小的球状颗粒,且其FTIR谱上仅剩余与硅氧振动相关的OH振动、SiO振动和Si-OH?Al振动,表明该残留物是以Si, Al, O为主要成分的非晶态物质,而残留物的XRF分析显示残留物中SiO<sub>2</sub>%的含量大于60%,表明360小时酸浸蚀残留物主要是非晶态的SiO<sub>2</sub>。粉红色残留物的漫反射NIR谱的研究显示2300nm附近的吸收峰随酸浸蚀时间的延长而模糊并消失,且1300nm~1600nm范围的吸收峰比未经酸浸蚀者的该区域吸收峰宽;灰白色坡缕石的漫反射NIR谱随酸浸蚀时间的延长未发生明显的变化。两个坡缕石随酸浸蚀时间延长在FTIR谱和NIR谱上的不同表现与化学成分的差异密切相关,粉红色者富镁,灰白色者贫镁。HCl对Mg<sup>2+</sup>的选择性溶出是导致二者离子浸出规律和残留物谱学特征差异的根本原因。酸活化4小时的1个贫镁坡缕石、2个富镁坡缕石和1个未活化粉红色坡缕石吸附铜后的EPR、FTIR和XPS研究显示:Cu<sup>2+</sup>在坡缕石中是被吸附在晶体结构的微空腔中、四面体片的单位六元环的底部或八面体位,结构微空腔中的铜是以[Cu(H<sub>2</sub>O)<sub>4</sub>]<sup>2+</sup>的形式被圈闭的。坡缕石表面吸附的铜是以两种价态存在的,在未活化坡缕石表面存在Cu<sup>2+</sup>和Cu<sup>+</sup>、酸活化坡缕石的表面仅存在Cu<sup>+</sup>,铜的窄扫描谱的拟合结果表明Cu是以和氧成键的方式被吸附在坡缕石的表面的。至于,铜在坡缕石表面为什么呈两种价态有待进一步的研究。也就是说,在坡缕石中铜是以四种形式存在的:1)坡缕石的表面,2)结构的微空腔中,3)四面体片的六方孔中,4)八面体位。饱满吸附铜的坡缕石的铜的解吸附实验显示Cu<sup>2+</sup>在不到0.25小时的时间内就在溶液中达到了平衡,且解吸附的量不足吸附量的1%,表明因被圈闭在结构通道的[Cu(H<sub>2</sub>O)<sub>4</sub>]<sup>2+</sup>、四面体片单位六元环底部和八面体位中的Cu<sup>2+</sup>,由于不易被H<sup>+</sup>触及,因而很难被解吸附,被解吸附的铜主要来自坡缕石的表面。Cu<sup>2+</sup>的解吸附表明坡缕石可以被用来治理被重金属离子污染的水体。

Based on systemic mineralogical study of two attapulgite clays from Jiangsu and Anhui Province, the pink and gray attapulgite clay which were collected from Guanshan deposit in Mingguang, Anhui Province, were selected to be purified for magnesium-rich and magnesium-poor palygorskite. The polycrystalline X-Ray Diffraction study show that the magnesium-rich palygorskite belongs to orthorhombic system, magnesium - poor palygorskite is a complex of monoclinic and orthorhombic ones. Magnesium-poor one is gray in color, and the other is pink. The R<sub>2</sub>/<sup>+</sup>R<sub>3</sub> ratios of octahedral layer are 1.4 for magnesium-poor palygorskite and 3.8 for magnesium-rich one. The FTIR and diffused NIR results has proved that the magnesium-rich palygorskite is a tri-octahedral mineral, and the magnesium-poor one is one kind of mineral intervened between tri-octahedral and di-octahedral. Systemic acid leaching experiments were carried on two magnesium-rich and magnesium -poor palygorskite. The results show that both palygorskite have the same trend for Si<sup>4+</sup> leaching, but the different leaching trend of octahedral cations can be seen in those two palygorskite during acid leaching process. As 1 mol/L HCl solution was employed, the Si<sup>4+</sup> concentration increased gradually. However at 3 and 5 mol/L HCl, the trends of Si<sup>4+</sup> concentration in leachate versus leaching time could be divided into 3 steps. For magnesim-poor palygorskite, the concentrations of octahedral cations are increasing with the increase of leaching time and the concentration of HCl solution. However, the same leaching trend was only seen in 1 mol/L HCl solutions for magnesium-rich palygorskite. It is obvious that three steps can be considered for magnesium-rich one. The conditionality of the leaching behavior of Mg<sup>2+</sup> and Si<sup>4+</sup> should be considered for the “characteristic three step trend” in 3 and 5 mol/L HCl solution for Si<sup>4+</sup> and magnesium-rich one. The Mg<sup>2+</sup>/(Al<sup>3++</sup>Fe<sup>3+</sup>) ratio increases steadily with leaching time and then reaches a constant value of 2 for magnesium-poor palygorskite, and >4 for magnesium-rich palygorskite in leached solution of 1 mol/L HCl. However as it leached by 3 and 5 mol/L HCl, the Mg<sup>2+</sup>/(Al<sup>3++</sup>Fe<sup>3+</sup>) ratio reaches a maximum value in a short time (<1.5 h), and then decreases to a constant value of 2 and 4. The different dissolution among different concentration of HCl solution indicates that the concentration has influenced the extraction rate of Mg<sup>2+</sup>. Based upon this fact, it is believed that at the earlier stage of dissolution by 1 mol/L HCl, the extraction of the cations is controlled by diffusion mechanism, i. e. the cations diffuse from the crystal surface to the solution, and the H<sup>+</sup> from solution to the surface. Initially, not only the octahedral cations, but also the tetrahedral cations with Al<sup>3+</sup> in tetrahedron site are exposed on the surface of the crystal. Therefore, the Mg<sup>2+</sup>/(Al<sup>3++</sup>Fe<sup>3+</sup>) ratio is lower. The chemical reaction gradually becomes a leading factor along with the developing of the dissolution. The preferential leaching of Mg<sup>2+</sup> results in the gradual increase of Mg<sup>2+</sup> concentration. The penetration of the H<sup>+</sup> from solution to the inner structural channels of the crystal makes the leaching throughout the channels, and the Mg<sup>2+</sup>/(Al<sup>3++</sup>Fe<sup>3+</sup>) ratio reach a constant value. In a word, two leaching state should be considered: diffusion mechanism and chemical reaction mechanism. The powder XRD results show that the solid leachate is still

palygorskite as the activating time less than 7 h. When leaching time is long enough to 360 h, the diffraction peaks become wider and split into several peaks. Finally, a big and large overlapped peak is formed at range of 20 to 30 $\theta$ . The microtopography of TEM and AFM show that more and more amorphous spherical particulate is formed along with leaching time. There is a large amount of amorphous spherical particulates in 360 h acid leached solid leachate. The amount of SiO<sub>2</sub> is bigger than 60% by XRF analysis. There is only absorption peak related to Si-O, Si-OH and Si-OH-Al in FTIR spectra. The above-mentioned facts suggest that the amorphous spherical particulate is amorphous silica. The bands near 2300nm become vague and fade away in the diffuse NIR spectra of pink relicts along with leaching time. The bands between 1300 and 1600nm of activated palygorskite are much wider than un-activated one. The diffuse spectra of unactivated and activated gray palygorskite are slightly different. The above-mentioned facts indicate that the different chemical composition brings the different spectra. The pink one is a magnesium-rich palygorskite, and the gray one is a magnesium-poor palygorskite. It is the different contents of Mg<sup>2+</sup> and the preferential selectivity of Mg<sup>2+</sup> that bring the different FTIR, NIR spectra and different activation mechanism. The EPR, FTIR spectra of a magnesium-rich palygorskite, 4 h acid activated two magnesium-rich ones and one magnesium-poor one indicate that the Cu<sup>2+</sup> is wrapped in the micro-channel of crystal structure and in the hexagonal cavities of Si-O sheet and a small fraction penetrate into the octahedral vacancies. XPS spectra show that two valences appear on the surface of un-activated palygorskite, and Cu<sup>+</sup> can be found on the surface of activated palygorskite. The further work should be carried to exoatiate on why two valences exist. In a word, there are four different occurrences of Cu ions in palygorskite: 1) adsorbed on the surface, 2) entering into the micro-channel of crystal structure, 3) adsorbing in the hexagonal cavities; and 4) penetrating into the octahedral vacancies. The desorbing experiment of Cu-adsorbed palygorskite indicates that the chemical equilibrium is reached less than 15 minutes. The amount of desorbed Cu<sup>2+</sup> is less than 1%. The above-mentioned facts suggest that the Cu<sup>2+</sup> ions wrapped in micro-channels, in hexagonal cavities, and in octahedral vacancies are not accessible to H<sup>+</sup>, difficult to be desorbed. The desorbed Cu<sup>2+</sup> ions come from the surface. It seems that the palygorskite is an outstanding materials to solve the polluted water environment.

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