



Natural Clay Mineral

일라이트(Illite)



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일라이트란(?)



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- 일라이트의 흡착/소멸 원리



일라이트의 쓰임

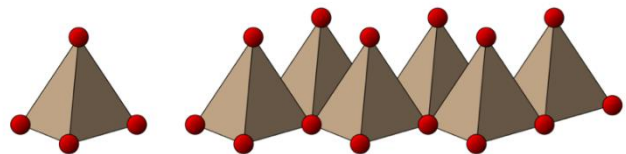
- 일라이트의 성질을 이용한 실생활 쓰임

일라이트(Illite)란?



일라이트(Illite)란?

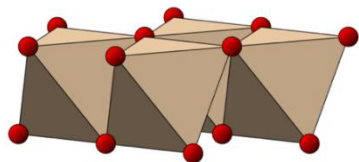
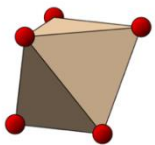
2 : 1형 점토 광물로서 운모 점토 광물이 풍화되는 동안 K, Mg 등이 용탈^{주1} 되어 생기는 비팽창형 광물. Si-O 사면체층이 서로 정점을 향하여 합친 두 층 사이를 Al(OH)₃의 팔면체층으로 이어 맞춘 **3층격자**를 단위로 하는 층상 점토 광물(Layered Clay Mineral) 화학조성은 (K,H₃O)(Al,Mg,Fe)₂(Si,Al)₄O₁₀[(OH)₂, (H₂O)]이며, 명칭은 미국 Illinois주 명칭에서 유래



Silica tetrahedra



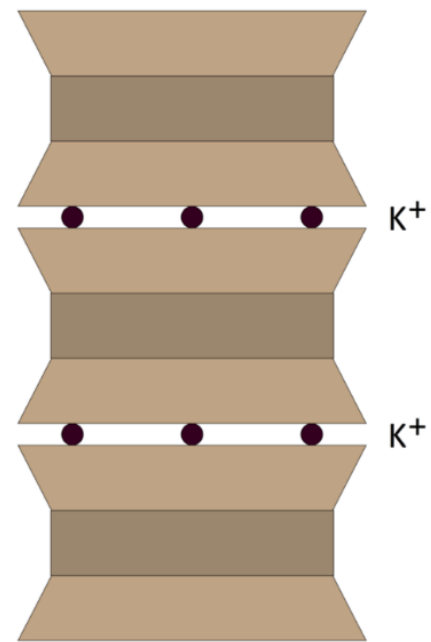
Schematic of silica layer



Alumina octahedra



Schematic of alumina layer

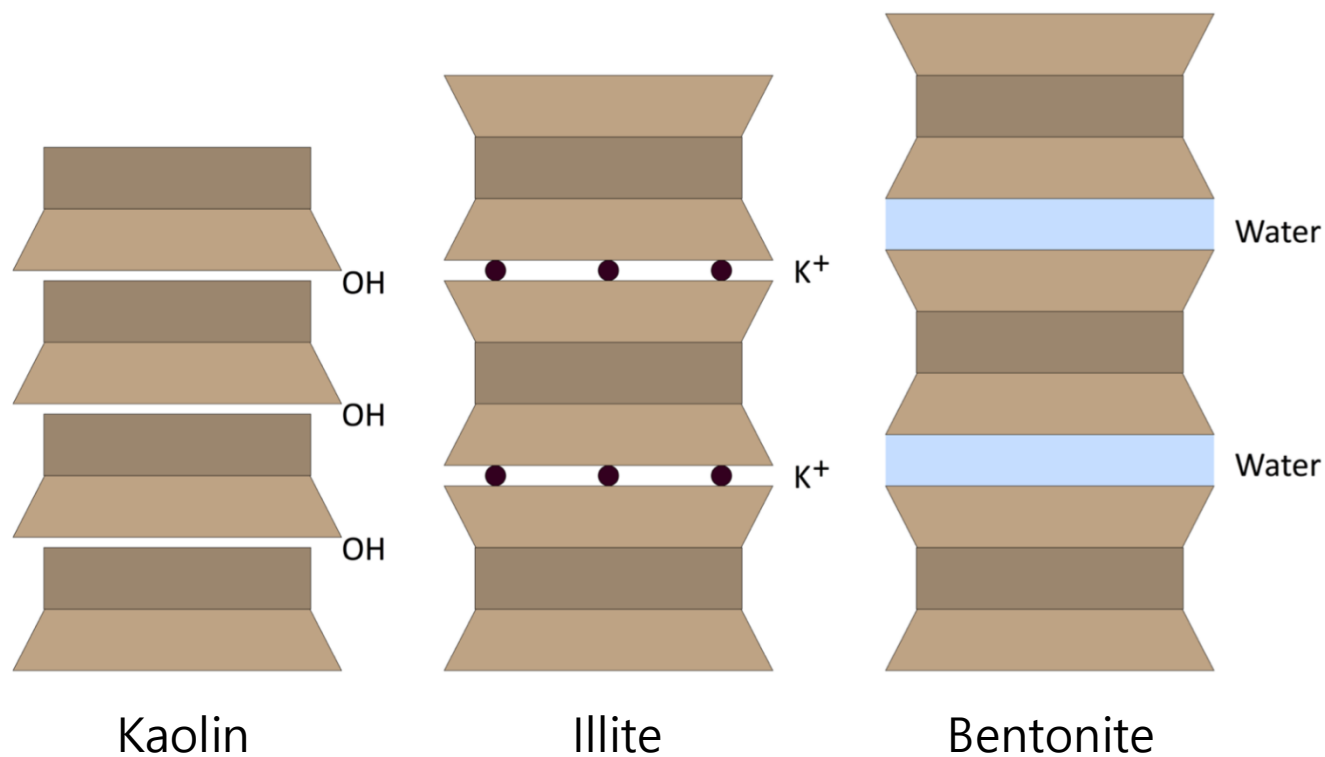


Illite

주1 : 토양 중에 침투한 물에 용해된 가용성 성분이 용액의 상태로 표층에서 하층으로 이동하거나 또는 토양 단면의 일정 깊이 아래로 제거되는 과정.

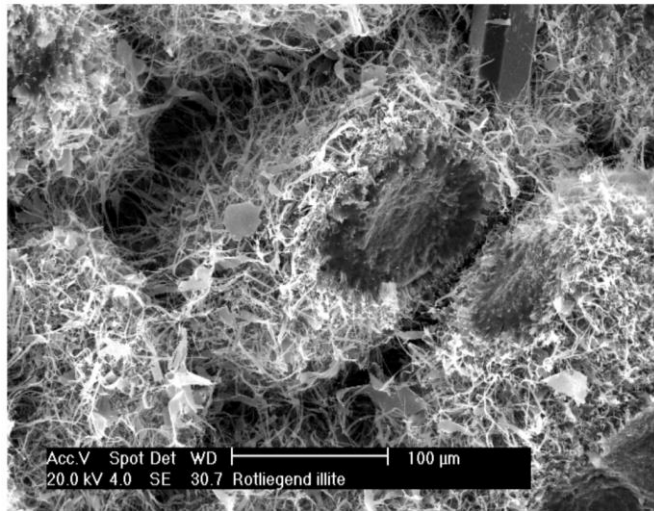
일라이트(Illite)의 Structural Property

일라이트는 백운모에 비하여 층 전하가 낮고, 그 전하는 4면체판의 Al^{3+} 과 Si^{4+} 의 동형치환 감소에 기인한다. 8면체판에서 약간의 동형치환이 일어난다. 일라이트는 층간에 존재하는 K^{+} 에 의한 강한 결합력으로 비팽창성이며 층 간격은 약 10\AA 이다

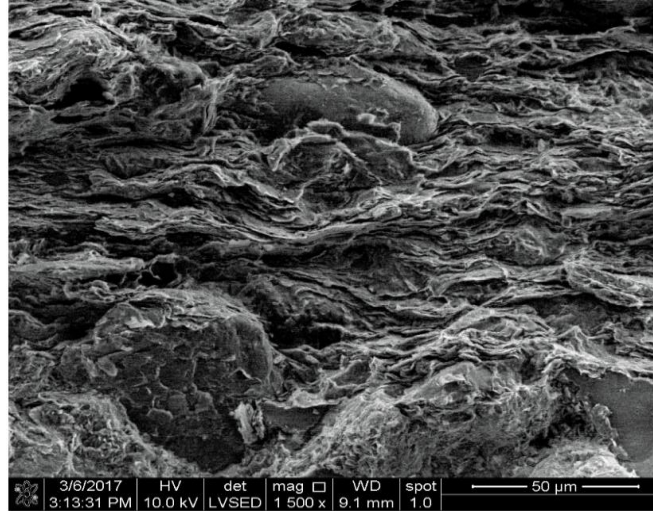


일라이트(Illite)의 Structural Property

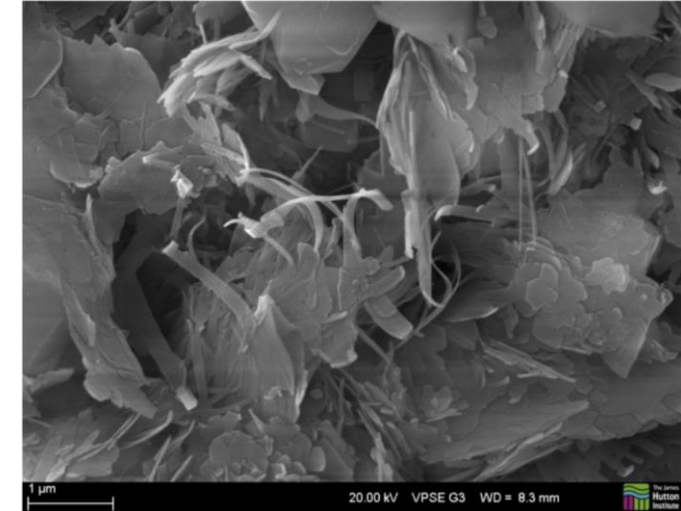
Electron micrographs of Illite



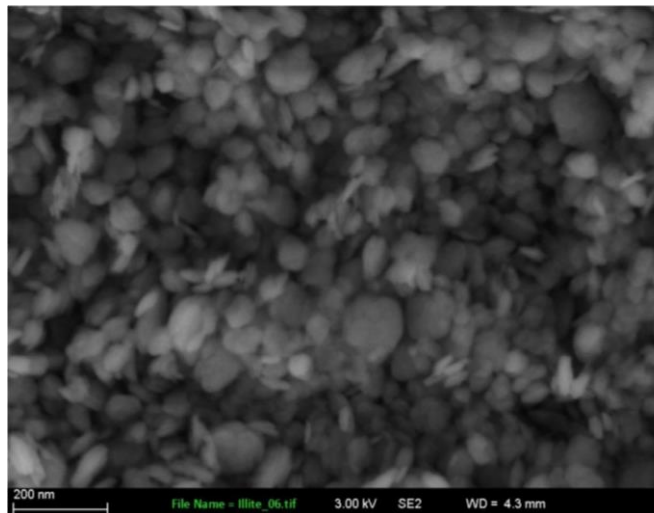
Fibrous illite, critical point-dried from methanol, Rotliegend Sandstone, North Sea



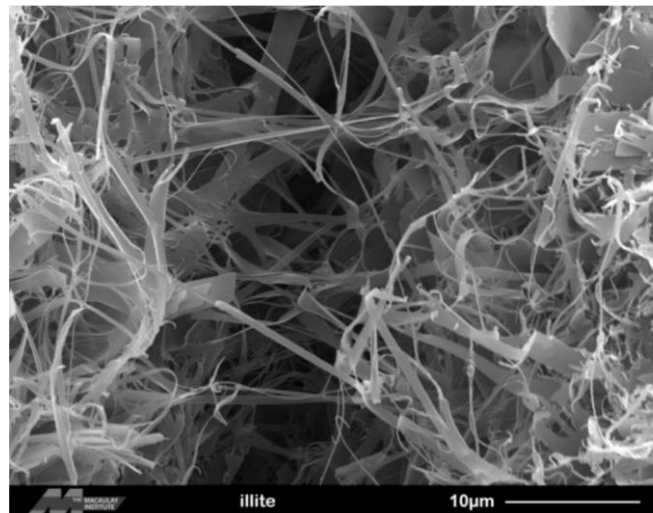
Illitic clay and zircon grain, Tar Springs Formation (Upper Mississippian, Chesterian Series), Illinois Basin



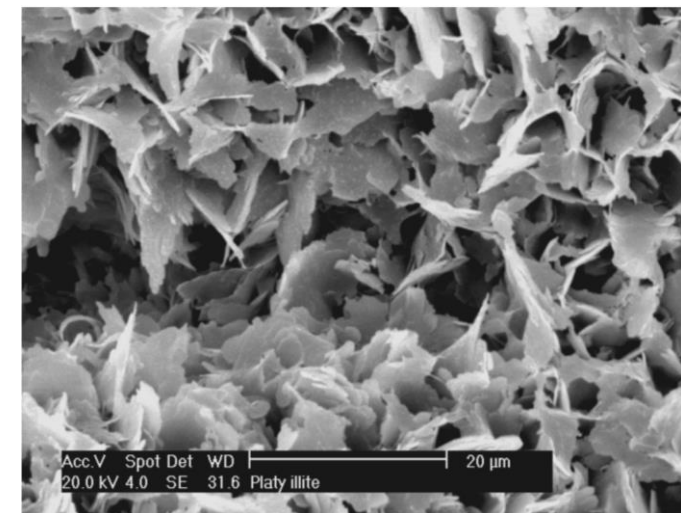
Mixture of fibrous and platy illite. Bone Spring formation, Permian Basin, USA



Small lozenge shaped crystals of the Fe-rich 'Muloorina Illite' from Muloorina, S. Australia



Fibrous illite, from: Rotliegend, S. North Sea



Platy Illite from the Rotliegend of Northern Germany

일라이트(Illite)의 효용성



중금속 흡착

유해 중금속, Pb, Ni, Cs,
Ti(l) 등을 흡착



피부 노폐물 제거

다공질의 특성을 이용해 피
부의 노폐물을 흡착하여 제
거

원적외선 방출

4~1,000um 파장의 원
적외선을 방출하여 야채
나 과일의 신선도 유지
및 세포 활성화



환경 불순물 제거

수질 환경에 있어 BOD,
COD등을 낮춰 수질을 개선



일라이트(Illite), 중금속 등 흡착·소멸 및 원리

일라이트의 불순물 제거
원리

넓은 비표면적
과 복잡한 기공
구조

Key Phrase

Clays and clay minerals have small particle size and complex porous structure with high specific surface area, which allows strong physical, chemical interactions with dissolved species.

These interactions are due to the electrostatic repulsion, crystallinity, and adsorption or specific cation exchange reactions.

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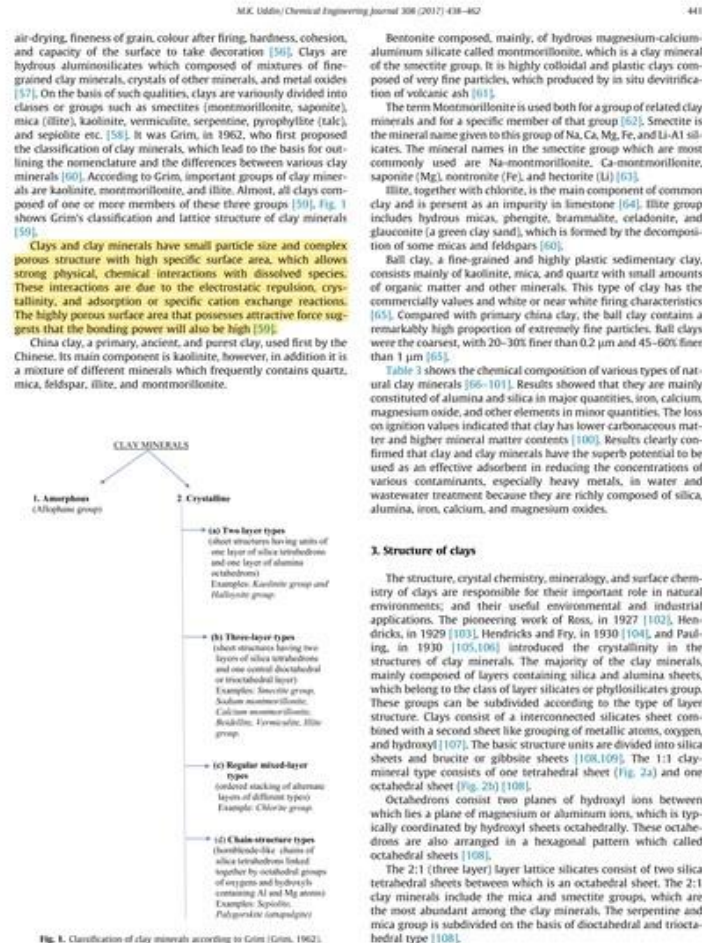
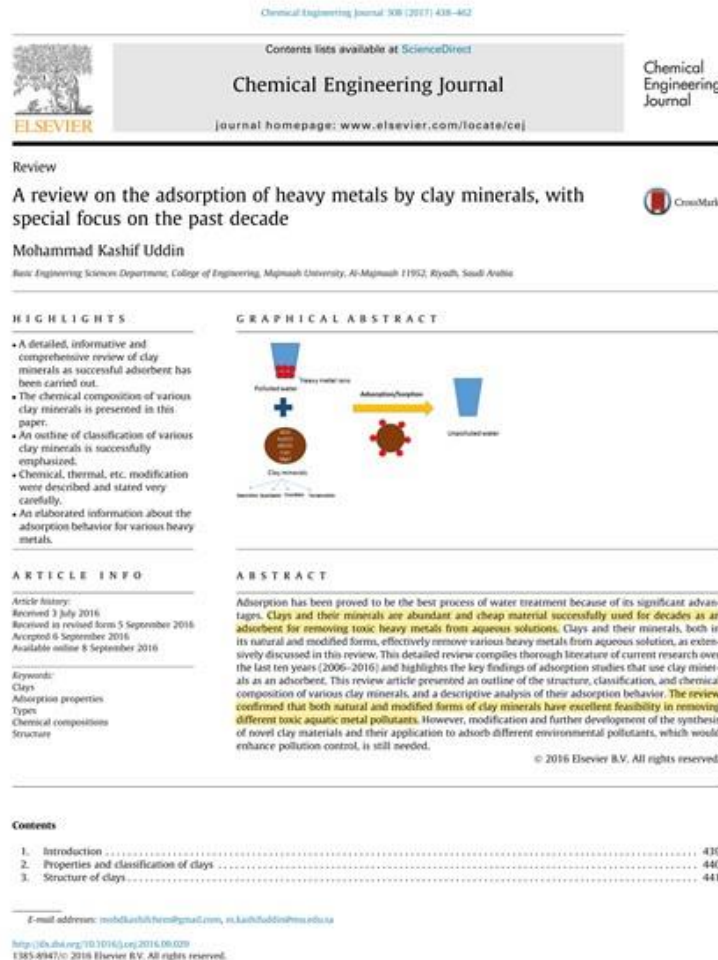
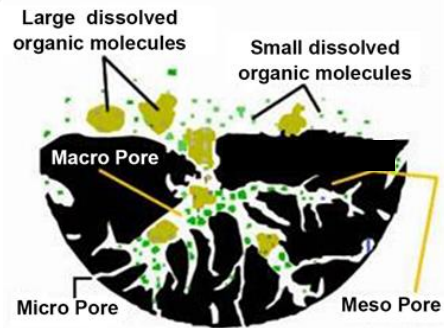


Fig. 1. Classification of clay minerals according to Grim (Grim, 1962).

일라이트(Illite), 중금속 등 흡착·소멸의 원리

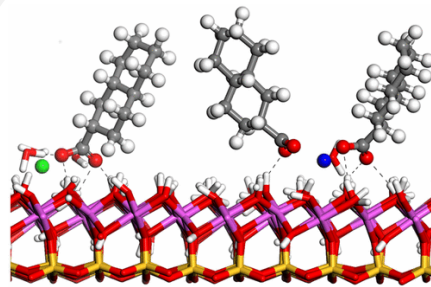
I



물리적 흡착

Capillary효과에 따른 기공 내 흡착

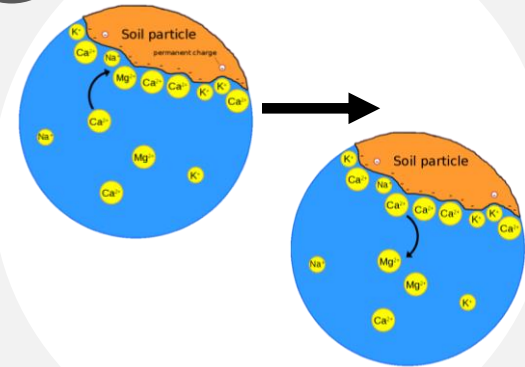
II



화학적 Binding

Cation and Organic pairing
에 hydrogen bonding

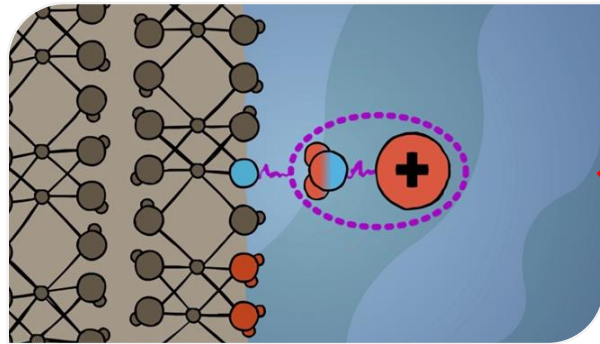
III



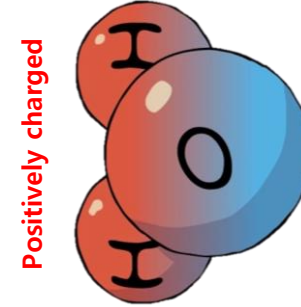
이온(Ion) Exchanging

양이온 교환능력에 따른 치환

일라이트(illite)의 물리·화학적 흡착

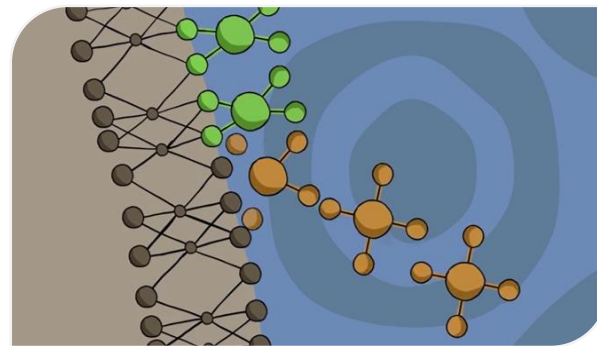
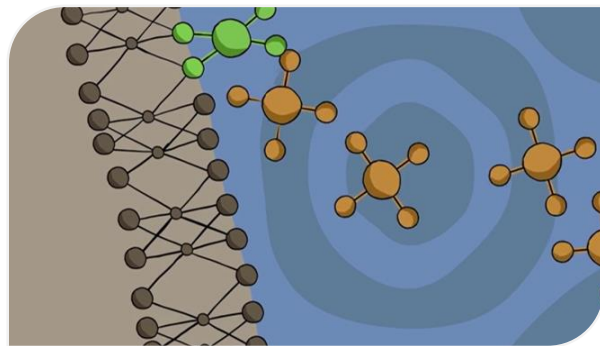


Anionic Clay +



+ Cationic Metal

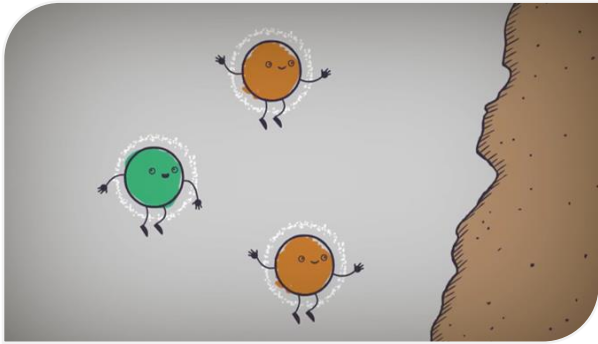
Electrostatic Interaction(Physi-sorption)
정전기적 힘에 의한 물리적 결합



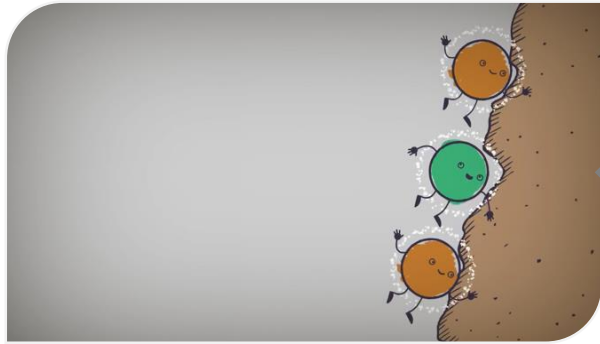
Chemical Interaction_Covalent bond
(Chemi-sorption)
공유결합을 통한 화학적 결합

일라이트(Illite)의 양이온 교환(Cation Exchange Process)

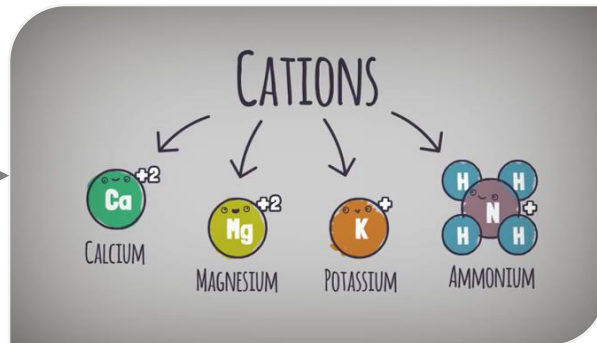
STEP. 1



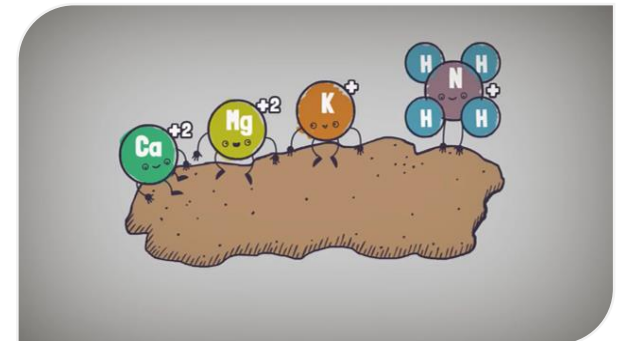
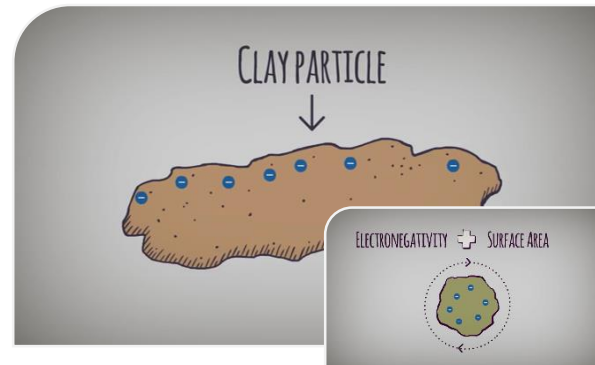
각각의 이온(Ion)들은 모두 정전기적에너지(Electrostatic Energy)를 가짐



일라이트와 같은 점토광물(Clay Mineral)에 잘 붙음

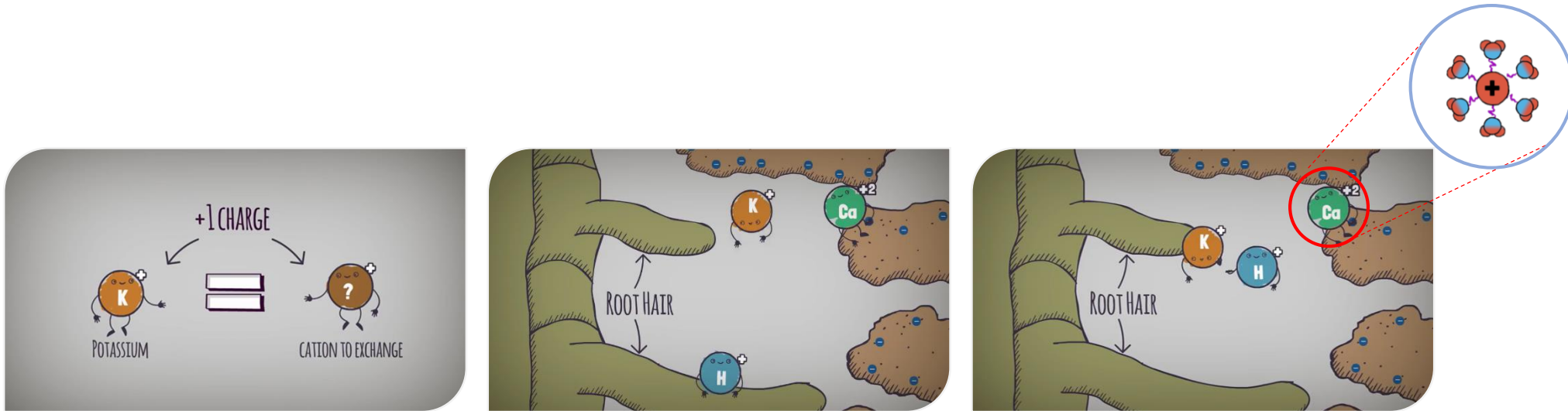


점토광물은 표면이 "- 전하"를 띠고 광물 이온은 '+ 전하'를 띠므로 정전기적 상호작용(Electrostatic interaction)이 발생

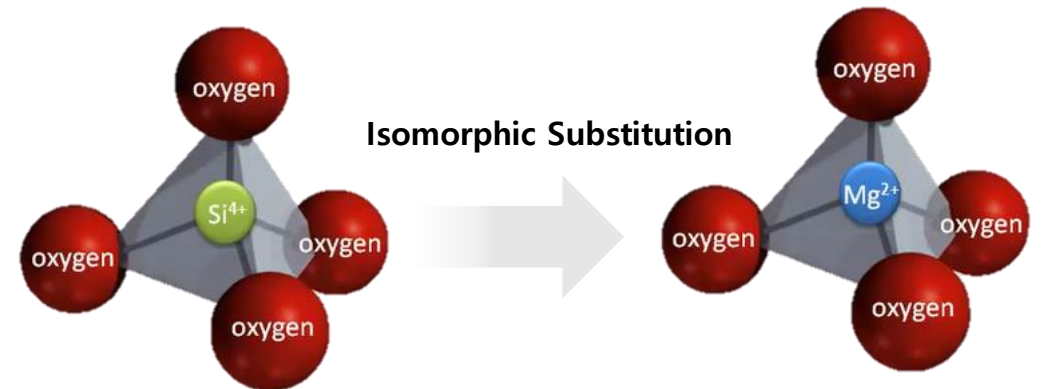


일라이트(Illite)의 양이온 교환(Cation Exchange Process)

STEP. 2



이때, 이온교환은 점토광물내에서 동종크기의 원자가 상호 치환으로 "양이온교환(Cation Exchange)가 일어남



동종치환(Isomorphic Substitution) : 점토광물(Clay Mineral)의 결정구조 변화 없이 유사 크기의 원자가 치환되는 현상

일라이트(Illite)의 Physical Property

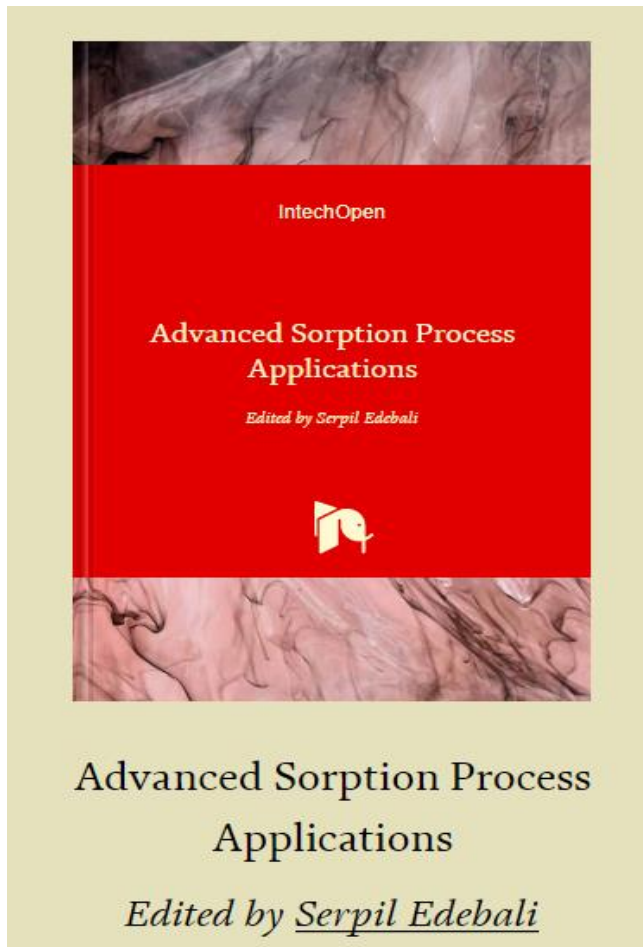
일라이트의 중금속 흡착

특히,
세슘, 탈륨
흡착

Key Phrase

Comparative study of Cs sorption on illite, montmorillonite and kaolinite show that Cs is most reactive and has strong affinity for illite compared to other clay

Chemistry, Published 2019,
DOI:10.5772/intechopen.80989



Sorption of Heavy Metals on Clay Minerals and Oxides: A Review
DOI: <http://dx.doi.org/10.5772/intechopen.80989>

illite, kaolinite and Kaolin, and has the higher affinity for Cd relative to other metals [68]. The sorption was at the maximum at pH 6 and 100% adsorption of 50 mg/L Cd. The sorption rate follows pseudo-first-order kinetics whereas the Langmuir model is used to describe the isotherm model [68]. Similarly, Pb(II), Cd(II), Ni(II) and Cu(II) sorption on kaolinitic clay from Longyan, China, show maximum sorption in 30 min and reduction of Pb concentration from 160.00 to 8.00 mg/L [69]. Another study found that adsorption of Cd(II), Co(II), Cu(II), Pb(II) and Ni(II) onto Acid treated kaolinite have great potential for removal these metals from aqueous solution compared to untreated kaolinite [70]. However, the use of natural and modified kaolinite clays for the removal of Cr(VI) for contaminated water is pH dependent and the adsorption increases from pH 1–2 at equilibration time of 240 min [71].

3.3 Illite

The adsorption of Caesium on clay made up of predominately of illite in the presence of small amount of organic matter and Fe-Oxide indicate that presence of organic matter play significant role for Cs uptake. The adsorption is described by Freundlich [48]. Maximum sorption of Caesium on to clay soil occurs at pH 8 and ambient temperature [72]. Comparative study of Cs sorption on illite, montmorillonite and kaolinite show that Cs is most reactive and has strong affinity for illite compared to other clay [73]. The sorption data was successfully modelled with 1-pK Diffuse layer model [73]. In another study, thallium is found to associate with illite in natural environment and sorption studies reveal that TI(I) sorbs more onto illite than smectite [74]. The affinity for TI follows this sequence: $\text{MnO}_2 > \text{illite} > \text{smectite} = \text{ferrihydrite} > \text{Al}_2\text{O}_3 = \text{goethite} > \text{SiO}_2$. However, in presence of Rb, Cs, TI adsorption to illite is less [74].

3.4 Bentonite

Removal of silver and copper in a binary solution containing the two ions with Verde-lodo bentonite reveals that the adsorbent has high adsorption affinity for copper than silver [75]. Cu adsorption on Verde-lodo bentonite is more at an elevated temperature and attained adsorption capacity of 0.110 mmol/g at 60°C, whereas silver attained 0.090 mmol/g at 20°C [75]. In another study, adsorption of indium on chitosan-coated bentonite is best described by Langmuir isotherm whereas the adsorption kinetics fits the pseudo second order [76]. Thorium (IV) sorption onto activated bentonite depends on temperature, pH, ionic strength, and type of anion and the adsorption kinetics can be described by pseudo-second-order model [77]. The activated bentonite is effective for removal of thorium (IV) and associates with it via surface complexation [77]. In the another study, bentonite was effectively used to remove thorium (IV) at pH 3, equilibration time of 18 h and 25°C and adsorption was fitted to Freundlich, Langmuir and Dubinin-Radushkevich isotherm models. Desorption experiment shows that thorium (IV) is best recovered with 1.0 M HNO_3 [49]. However, the use of bentonite for sorption of heavy metals has some negative effect. This is because increase in concentration of heavy metals such as zinc, lead and copper results to decrease in liquid limit, swelling potential, swelling pressure and free swelling of bentonite but increases its hydraulic conductivity due to sorption of heavy metal in the double layer structure [78].

3.5 Natural clay

Competitive adsorption and desorption cadmium, chromium, copper, lead and zinc on natural clay show difference in the optimum maximum pH of adsorption

Chemistry, Published 2019, DOI:10.5772/intechopen.80989
Sorption of Heavy Metals on Clay Minerals and Oxides: A Review
Ifeoma Mary Ugwu, Onyedikachi Anthony Igboke

일라이트(Illite)의 Physical Property

기능성 무기물과 폴리에틸렌계 수지의 정량적 혼합시스템에 의한
환경대응형 포장소재 개발

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Environment Corresponding Package by Quantitative Mixing System
with Functional Inorganic Material and Polyolefin Resin

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Abstract—A lot of research has been made over the recent decade to develop testing packages with antimicrobial properties to improve food safety. In this study, a new method, experimental device and technology for environmental corresponding packages of polypropylene (PP) film has been developed to provide effective temperature buffering during the transport/long-term storage of grains or foodstuffs from the supplier to the market. This quantitatively optimized mixing system enabled to produce PP films with the 700-1,400μ (width:1.5-3mm, thickness:0.01-0.5mm). In the whole mixing systems, the finely-granulated inorganic illite and PP virgin chip for master batch (M/B) chip was calculated by digital measurement methods, and then the M/B chip for PP film was adapted through a air jet and PP grinding method. The prepared PP film was characterized with tensile strength and elongation, far infrared radiation (FIR) emissivity, antimicrobial activity and deodorization properties. The results revealed that the two differently grain-sized illite could be show homogeneously dispersed on PP chip surface, and as the increasing of illite content, the FIR emissivity and the anion emission rate of film was increasingly improved. In both of 325 and 1,500 mesh-sized illite contained PP chip, of course the antimicrobial activity was good. But the ultimate deodorization rate for ammonia gas of PP film were found to be approximately the same.

Keywords: polypropylene film, illite, functional inorganic material, master batch chip, quantitative mixing system

1. 서 론

FTA 협정으로 국내의 농수산물의 자유로운 수출입 시대에 이르면서 장기적인 보관 및 유통과정에서 부패를 방지하고 신선도 및 품질을 안정시키기 위해 다양한 형태의 저장, 유통용 포장재가 요구된다. 따라서 상대적으로 저렴한 수입 농산물에 대응할 수 있는 효과적인 고품질 전략의 일환으로 다기능성 폴리프로필렌(PP) 및 폴리에틸렌과 같은 고분자필름을 이용하는 방법이 이를 실현할 수 있을 것으로 기대된다. 그 중 PP는 고분자량과 고결정성의 강한 소재로서, 산과 알칼리에 대한 내성,

열적안정성, 항균성 등이 뛰어난 반면, 분자구조 내 다량의 메틸기로 인해 친수성이 낮아, 젖음성(0.05% at 20℃) 및 염색성이 불량하며, 탄소원자에 부가된 수소원자들은 산소나 오존의 공격을 받기 쉬워 산화에 대한 저항성이 떨어지며, 수지의 가공온도가 높은 등의 단점이 있어 현재까지 의류 및 다른 산업으로의 응용에 어려움이 있었다^[1].

따라서 나일론이나 폴리에스테르와 같이 의류용으로 개발되는 대신, 뛰어난 투명성, 기계적 강도, 내열성이 요구되는 포장용 필름재료로서 주로 사용되어 왔다. 국내에서는 1980년대부터 PP수지의 이용이 증가되어, 이 후 세계적인 섬유산업의 흐름이

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김희삼 · 임현주 · 박영미

Table 5. Deodorization of functional PP film

Time (min)	Initial Conc. (ppm)	325 mesh				1500 mesh			
		3%	5%	7%	10%	3%	5%	7%	10%
0	200	151	151	149	147	149	147	146	144
30	176	141	140	137	137	139	137	136	135
60	169	125	124	122	122	124	122	121	120
120	145	118	117	115	115	117	115	114	114

인할 수 있으나, 7%이상에서는 효과가 더 이상 증가하지 않음을 알 수 있다. 또한 1,500mesh의 일라이트를 함유한 PP필름의 탈취성이 325mesh의 일라이트를 함유한 필름보다 더 좋은 것을 알 수 있다. 그러나 탈취효과는 70-98%에 못 미치는 것을 알 수 있다. 같은 양의 일라이트를 함유한 폴리에스터(PET) 필름의 탈취성을 비교테스트 해보았을 때는 70%이상 효과를 얻을 수 있었으나^[10], PP 필름은 탈취성이 20% 정도로서 그다지 만족스럽지 못한 결과를 나타내고 있다. 이는 PET와 PP의 분자구조와 표면적 차이에 기인하는 것이라 사료된다. 즉, 암모니아의 질소원자가 반응할 수 있는 기회는 탄화수소로 이루어진 강력한 PP에 비해 PET가 더 유리함을 시사하며, 표면에 있어서는 알의 흡이 온방출량 및 항균성 결과에서와 마찬가지로 입도가 작은 일라이트가 혼합된 PP 필름이 더 많은 표면적을 제공함으로써 탈취성도 동일한 결과를 얻을 수 있었다. 이러한 결과는 서론에서 이미 제시한 바와 같이 일라이트 본래의 기능인 탈취, 축열 및 항균 성능을 매우 잘 반영한 것으로 사료된다.

4. 결 론

친환경 식품용 포장재를 개발하기 위해 PP 칩에 일라이트를 혼합하는 과정에서 기존의 복잡하고 비경제적인 제조방법을 대안할 수 있는 장치를 마련하였으며, 제조된 PP 필름의 물성을 평가하였다. 원적외선 및 음이온 방출, 항균, 항곰팡이 및 방출성, 탈취성 등 식품 및 곡물류의 운반/포장에 요구되는 특성을 얻기 위해 본 연구에서 사용된 일라이트가 매우 적절함을 확인할 수 있었다. 일라이트를 함유한 기능성 PP 필름은 일라이트와 virgin PP 칩을 정량적으로 균일하게 혼합할 수 있는 새로운 시스템에 의해 이루어졌는데, 즉, 이 시스템을 이용하여 입도가 다른 325mesh와 1,500mesh 두 종류의 일라이트와 zinc stearate와 wax를 일정비율로 혼합하여 PP 필름과 50%의 일라이트가 균일하게 분포

된 M/B 칩을 개발할 수 있었다. 일라이트의 입도에 상관없이 함량이 10%이상 초과되면 일라이트 자체의 물성 때문에 필름형성이 곤란하였다. 물성 시험결과, 1,500mesh의 일라이트가 함유된 필름이 325mesh 일라이트가 함유된 필름보다 물리적 성질이 우수함을 알 수 있었으며, 함량이 높을수록 항균성능이 향상되는 것을 확인할 수 있었다. 7%와 10%의 일라이트가 함유된 필름의 물성은 눈에 띄게 큰 차이는 없었기 때문에 상용화시에는 1,500 mesh 일라이트가 7% 가량 함유된 PP필름을 제조하는 것이 가장 효율적일 것으로 보이며, 또한 필름뿐만 아니라 필라멘트 역시 방사할 때 M/B 칩에 1,500mesh의 일라이트를 1-7% 범위 내에서 첨가한다면 고기능성의 PP 필라멘트를 얻을 수 있을 것으로 사료된다.

감사의 글

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일라이트의 기능 및 응용

원적외선 및 음

이온 방출/

항균, 탈취 (암모니아) 능

Key Phrase

4~1,000μm의 원적외선 방출은 야채나 과일의 신선도 유지, 실내공기 정화, 물의 정수 및 활성화, 신진대사 촉진, 살균 및 방충, 등 채소 및 과일의 맛과 영양보존 등의 다양한 기능

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일라이트(Illite)의 Physical Property

일라이트의 기능 및 응용



Research paper

Caesium incorporation and retention in illite interlayers

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ABSTRACT

Radioactive caesium (chiefly ¹³⁷Cs) is a major environmental pollutant. The mobility of Cs in temperate soils is primarily controlled by sorption onto clay minerals, particularly the frayed edges of illite interlayers. This paper investigates the adsorption of Cs to illite at the molecular scale, over both the short and long term. Transmission electron microscopy (TEM) images showed that after initial adsorption into the frayed edges, Cs migrated into the illite interlayer becoming incorporated within the mineral structure. Caesium initially exchanged with hydrated Ca at the frayed edges, causing them to collapse. This process was irreversible as Cs held in the collapsed interlayers was not exchangeable with Ca. Over the long term Cs did not remain at the edge of the illite crystals, but diffused into the interlayers by exchange with K. Results from extended X-ray absorption fine structure spectroscopy (EXAFS) and density functional theory modelling confirmed that Cs was incorporated into the illite interlayer and revealed its bonding environment.

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1. Introduction

The ubiquity of ¹³⁷Cs in nuclear waste means that it is one of the most common radionuclides released into the environment by human action. Once released, the relatively long half-life ($t_{1/2}$ 30 years) and large dose rate of ¹³⁷Cs mean that it poses a potential long term radiation risk. The nuclear accidents at Chernobyl, and more recently at Fukushima, demonstrated this most acutely. In both these cases, radiocaesium remains the key contributor to radioactive dose and the reason for maintaining the exclusion zone (Jacob et al., 2009; Kinoshita et al., 2011). Additionally ¹³⁷Cs is a common contaminant at nuclear sites, such as Hanford and Sellafield, due to historic releases (Chorover et al., 2008; Reeve and Ellcock, 2009).

Caesium is highly soluble and is present in groundwater as the monovalent Cs⁺ cation under all conditions of Eh and pH. Due to this, its concentration in solution (and thus its environmental mobility) is primarily controlled by retention on the surfaces of soil minerals, primarily through cation exchange (Sawhney, 1972; Cornell, 1993;

Hird et al., 1996). Caesium does not readily adsorb onto iron oxide minerals (Todorovic et al., 1992; Wang et al., 2000) and it is therefore principally adsorbed on clay mineral surfaces (especially in organic poor soils) (Grueter et al., 1990; Shenber and Eriksson, 1993b; Chibowski and Zygmunt, 2002). However, the sorption behaviour of Cs varies greatly between the different clay minerals and the different exchange sites on those clays. Caesium adsorption to clays occurs via several different mechanisms, including outer-sphere adsorption to planar surfaces, edge adsorption and intercalation into structural sites (Jacobs and Tamura, 1960; Hird et al., 1996; Bradbury and Baeyens, 2000). Here, and throughout this paper, outer-sphere adsorption is defined as electrostatic bonding of a hydrated ion to a surface, inner-sphere adsorption as direct bonding (electrostatic or covalent) of the dehydrated ion to the surface reactive site and absorption as incorporation into the clay structure (including within a collapsed interlayer). The dominant adsorption process within a particular environment, is dependent on a number of factors, including Cs concentration, clay structure and solution pH (Fuller et al., 2014). Multiple studies have shown that Cs is preferentially removed from solution and retained on the surfaces of soil minerals even when the total ionic strength of other cations is very high (Brouwer et al., 1983; Dyer et al., 2000; Chorover et al., 2008). Studies from soils with varying mineralogy showed that this selective adsorption and retention of Cs was occurring primarily on illite

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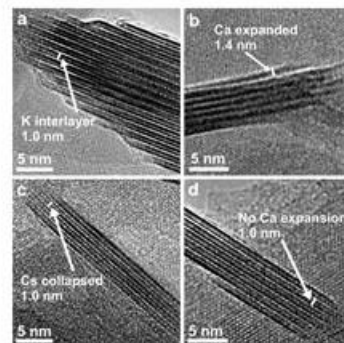


Fig. 1. Expansion and collapse of the illite interlayer: (a) The initial illite material shows a stable 1.0 nm basal spacing. (b) The edge of the illite exposed to 1.4 nm upon sorption of Ca. (c) Exchange of the edge sorbed Ca for Cs causes a dehydration and re-collapse of the interlayer. (d) Cs held in this collapsed interlayer was not exchanged by Ca and the structure did not re-expand.

in deionised water for 4 months and there was no detectable reduction in K concentration (SI section S2 and Figs. S2 and S3). However, when the illite was suspended in CaCl₂ the edges of the crystals expanded, giving a basal spacing of 1.4 nm (Fig. 1b). EDX confirmed that there was Ca present in these expanded edge regions and that they were deficient in K, relative to the original material (SI Fig. S4b). This frayed edge region extended up to 5 nm into the interlayer. Fig. 1a and b shows the well documented mechanism of illite weathering which liberates the interlayer K ions (Jackson and Doring, 1979; Sparks and Huang, 1985; Moritsuka et al., 2004) and causes the formation of the frayed edge sites. The 1.4 nm spacing is only possible if the Ca remains in hydrated outer-sphere complexes, where it is easily exchanged (Comans et al., 1991; Nakao et al., 2008). Therefore the frayed edges are more hydrated than the stable K-illite interlayers.

Once the illite had been successfully weathered with Ca and 'frayed edges' formed it was possible to investigate the absorption of Cs into the 'frayed edge'. Fig. 1c shows that after suspension of the Ca-illite in Cs for one month the edges had recollapsed from 1.4 nm to 1.0 nm. After this treatment no Ca was detected in the edges by EDX (SI Fig. S4c). Instead, a small concentration of Cs was detected in the structure. Therefore it can be asserted that the Cs was absorbed into the frayed edge site via cation exchange with the Ca ions. This exchange caused the edges to collapse back down to 1.0 nm. This likely occurred due to dehydration of the interlayer space as Cs is less strongly hydrated than Ca (Rosso et al., 2001). This mechanism of expansion and collapse has been proposed for many decades in both the radiochemistry and mineral weathering literature (Jackson et al., 1952; Sawhney, 1967; Benedicto et al., 2014). In this current work this process is observed to be occurring with Cs in illite. To investigate the reversibility of this Cs absorption, the samples were resuspended in a Ca solution to attempt to re-expand the Cs-interlayers with Ca. However this appeared to be unsuccessful. No Ca sorption was detected in EDX chemical analysis (SI Fig. S4d) and Fig. 1d shows that the structure remained unexpanded at 1.0 nm. This unexpandable nature of the Cs-interlayer was proposed by de Koning and Comans (2004) as a likely explanation for irreversibility of Cs absorption into illite. This lack of Cs desorption from illite has been widely

observed (Shenber and Eriksson, 1993a; Bellenger and Staunton, 2008; Gil-García et al., 2008) and attributed to specific retention in the frayed edges (Williams et al., 2004). The new results presented here confirmed this lack of re-expansion of the collapsed frayed edges and offer an explanation for the irreversibility of Cs absorption, even after short contact periods, consistent with de Koning and Comans (2004).

3.2. Long term Cs interlayer incorporation

Beyond the short term absorption of Cs to expanded Ca-interlayers it is important to understand the long term fate of Cs in the collapsed K-interlayer region. Cs absorption can take over a year to reach equilibrium (Sawhney, 1966; Comans et al., 1991; Comans and Hockley, 1992; Konoplev et al., 1996; Poissot et al., 1999) so it was crucial to study the progress of illite incorporation over this timescale. Fig. 2 presents High Angle Annular Dark Field (HAADF) STEM micrographs of illite viewed along the clay layers at different stages during the process of Cs absorption. Assuming uniform thickness, the intensity of the HAADF image is proportional to the square of the mean atomic number; allowing layers with different compositions within the clay structure to be identified. Specifically in the natural illite starting material (Fig. 2a) EDX analysis (SI Fig. S5a) confirmed that the structure consisted dominantly of Si (Z = 14), Al (Z = 13) and O (Z = 8) atoms in the 2:1 layers and K (Z = 19) in the interlayer. However, the 2:1 layers appear brighter than the interlayer due to significant Fe (Z = 26) substitution in the octahedral sheet. In contrast, HAADF images of the samples exposed to Cs for 4 or 7 months showed interlayer spaces that varied in intensity, even within a single crystal (Fig. 2b and c). In these samples a number of the interlayers were brighter than the 2:1 layers (Fig. 2b). Additionally in some of the illite crystallites a single interlayer was partially brighter than the 2:1 layer and partially darker (Fig. 2c). The brightness in these interlayers indicates that the mean atomic number (Z) is greater than either the 2:1 layers or the darker interlayers. Caesium (Z = 55) will give higher intensity than either K (Z = 19) or the Fe (Z = 26) in the 2:1 layers in a HAADF image, suggesting that these bright interlayers contain Cs. The presence of Cs in both of these samples was also confirmed by EDX (SI Fig. S5b). This phenomenon of heterogeneous interlayer filling was also observed by Okumura et al. (2014) for Cs incorporation into phlogopite. The reason for this heterogeneous distribution of Cs between interlayers is unclear but may be due to variation in layer charge on the aluminosilicate 2:1 layers leading to a difference in Cs/K exchange rates. Once exchange has begun the interlayer provides a fast diffusion path, meaning it is then possible for the Cs ions to diffuse into and exchange the whole interlayer space to attain the energetically more favourable Cs substituted structure (Rosso et al., 2001). Alternatively, Cs may be absorbed into vacant interlayer sites (rather than exchanged with K) that are present in these interlayer spaces, but not in others. By 12 months the majority of the interlayers in the imaged sample appear to be bright, consistent with them being Cs filled (Fig. 2d). An EDX analysis of the 12 month sample also showed significant concentrations of Cs in the structure (SI Fig. S5d and Table S1).

In addition to the phase contrast and EDX evidence for the incorporation of Cs into the interlayer space the effect of changing interlayer cation on the mineral structure was also examined. To determine this change, a large number of unit layers (2:1 layer and interlayer space), with both dark (n = 180) and bright (n = 31) interlayers, were measured. Fig. 2e shows the range and frequency of measured basal spacings. From these results it was determined that the basal spacing of those regions with brighter interlayers was on average 0.07 nm larger than the less bright interlayers (Fig. 2e), showing a significant expansion (Mann Whitney U; p < 0.001). Density functional theory modelling was then used to determine if these basal spacings, and the associated change, were caused by the exchange of K for Cs in the interlayer site. A density function theory model was constructed with either K or Cs in the interlayer site. The modelling was performed using both the local density approximation (LDA) and the generalised gradient

세슘 흡착

Key Phrase

once caesium is adsorbed into the frayed edge sites it cannot be readily desorbed back to solution, controlling the long term retention of Cs in the environment,

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일라이트(Illite)의 Physical Property

일라이트의 유기 오염물
흡착

COD : 86%

BOD : 71.86%

저감

Key Phrase

The experimental results revealed that the rate of adsorption of organic compounds increased gradually with the increase for clay used.

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ELIMINATION OF ORGANIC POLLUTANTS FROM URBAN WASTEWATER BY ILLITE-KAOLINITE LOCAL CLAY FROM SOUTH-EAST OF ALGERIA

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ABSTRACT

The main purpose of the present study is the identification of the physicochemical characteristics of local clay from a southeast province of Algeria (El Oued) and its use in wastewater treatment for the removal of organic pollutants. Obtained granules were characterized different physico-chemical methods. X-ray diffraction shows a majority composition of illite, moderately of kaolinite and minority of quartz. FTIR showed the presence of all the characteristics peaks of the studied clay. BET method reveals a specific area of about 110 m²/g. SEM shows irregular shapes with ragged edges. The value of CEC is about 20.416 mmol/100g. The agitation speed of 625rpm, contact time of 150min, pH of 8.5, and clay mass of 2g and operatory temperature of 30°C were fixed as the optimal conditions of the wastewater treatment. These optimal conditions showed a good elimination results by reducing COD, BOD5, and SS with removal rates of 86%, 71.86%, and 52.17% respectively.

KEYWORDS: Clay, Wastewater, Organic pollutants, Algeria.

1. Introduction

Clay is used as a rock term and as a particle-size term in the mechanical analysis of sedimentary rocks, soils, etc. As a rock term, it is difficult to define precisely, because of the wide variety of materials that have been called clays. Clay refers to a naturally occurring material composed primarily of fine-grained minerals. The minerals found in clay are generally silicates less than 2 microns in size (Fukushi et al., 2014; Markov et al., 2005; Erdemoglu et al., 2004).

The interest given in recent years to the study of clays by numerous laboratories throughout the world is justified by their abundance in nature, their low cost, and the presence of electrical charges on their surfaces and, above all, the exchangeability of the interfoliar cations. All these properties make clay a material of exceptional quality (Toubtough et al., 2014). Several previous works (Ayu et al, 2017; Mervette & Fatma, 2016; Khan, 2017; Mohammad Kashif Uddin, 2017; Mazloomi & Jalali, 2017;

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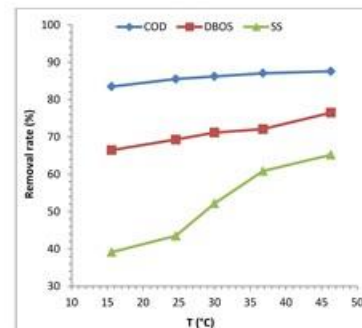


Figure 5 Variation of removal rates of COD, BOD5 and SS depending on temperature

4. CONCLUSION

Clays have been utilized as an adsorbent and as an ion-exchange material for the removal of ions and organics due to their low cost, natural abundance, high adsorption capacity, and ion-exchangeable property.

The Granulometric analysis study showed that the soil contains 42% clay minerals; the latter contains mostly illite, some kaolinite and a bit of quartz, and has a specific surface area 110.786 m²/g and has also a cation exchange capacity of 20.416 mEq/100g.

These properties enable the clay to be used for the removal of organic pollutants in significant amounts of urban wastewater. For that reason it was sought to find the optimal conditions for the removal of organic pollutants to obtain water that has standards that make it suitable for agricultural and industrial use.

By studying the factors affecting adsorption (speed of stirring, contact time, pH, clay mass and temperature) it is possible to select optimal conditions for reducing organic pollutants by adding a concentration of 3.33 g/L with an acidity of around 8.5. The operation is carried out at 30 °C near normal temperature and 625 rpm for 150 minutes.

일라이트(Illite)의 Physical Property

일라이트의 납(Pb) 흡착



Article

Effective Removal of Lead Ions from Aqueous Solution Using Nano Illite/Smectite Clay: Isotherm, Kinetic, and Thermodynamic Modeling of Adsorption

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Abstract: Illite-smectite clay is a new mixed mineral of illite and montmorillonite. The ability of nano illite/smectite clay to remove Pb(II) from slightly polluted aqueous solutions has been investigated. The effects of pH, contact time, initial concentration of Pb(II), nano illite/smectite clay dosage, and temperature on the adsorption process were studied. The nano illite/smectite clay was characterized by X-Ray Diffraction (XRD), Fourier transform infrared spectrometry (FTIR), and Scanning electron microscopy (SEM). The results showed that Pb(II) was adsorbed efficiently by nano illite/smectite clay in aqueous solution. The pseudo-second-order kinetic model best described the kinetic of the adsorption, and the adsorption capacity of nano illite/smectite (I-S_m) clay was found to be 256.41 µg·g⁻¹ for Pb(II). The adsorption patterns followed the Langmuir isotherm model. Thermodynamic parameters, including the Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) changes, indicated that the present adsorption process was feasible, spontaneous, and endothermic in the temperature range of 298–333 K.

Keywords: Pb(II); nano illite/smectite clay; adsorption kinetics; adsorption thermodynamic

1. Introduction

Water is a source of life. In recent years, a large number of studies have indicated that the water, especially of rivers, in urban areas has been seriously contaminated by heavy metals [1–3]. Because heavy metals are not readily degradable in nature and accumulate in animals as well as human bodies, people who drink water or eat food containing heavy metals for a long time are susceptible to disease. Therefore, heavy metal contamination in the water environment has attracted great concern owing to its environmental toxicity and persistence.

Lead is a widely distributed and accumulative pollutant, and is the third-most common toxic element in the heavy metal toxicity list. It is also one of the 10 chemicals that the World Health Organization (WHO) has set out as a cause for significant public health concerns. Once the lead in the environment through various ways enters the human body and accumulates, the nerve, digestive, immune, and reproductive systems will be compromised and the health of human beings will be threatened, especially that of children [4,5]. The permissible limit for lead in potable water is 0.01 mg·L⁻¹ [6]. The removal of Pb(II) has become a great concern globally due to these toxic effects of Pb(II) on living beings. In the past few years, various techniques have been used, such as chemical

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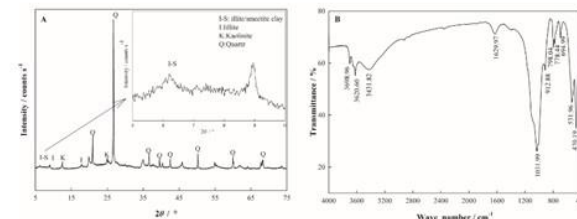


Figure 1. XRD spectra (A) and FT-IR spectrum (B) of nano I-S_m.

SEM analysis is another important tool used in the determination of the surface morphology of an adsorbent. In this study, SEM was used to probe the change in morphological features of nano I-S_m and Pb-adsorbed nano I-S_m (Figure 2).

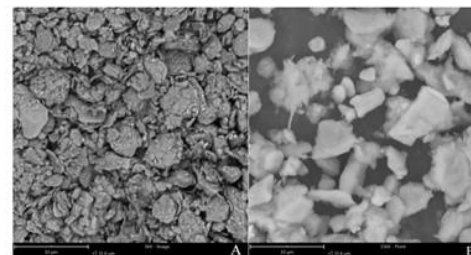


Figure 2. (A) SEM micrograph of nano I-S_m (before adsorption); (B) after Pb(II) adsorption.

3.2. Effect of Adsorption Conditions

3.2.1. Effect of pH

The effect of pH on Pb(II) removal rate was investigated at 298 K for 60 min as shown in Figure 3A. It was observed that the levels of adsorption efficiency of Pb(II) increased significantly with increasing pH. The removal rate of Pb(II) on nano I-S_m was only 41.25 % at pH 2.0. In addition, the removal rate of Pb(II) tended to equilibrate at pH 4.0. When the solution had a pH > 6.0, the solution of Pb(II) gradually formed Pb(OH)₂ precipitate, and the solution system became relatively complex.

중금속; 납(Pb)
흡착

Key Phrase

adsorption mechanism was predominant for the adsorption of Pb(II) on nano I-Sm. The saturated adsorption capacity of Pb(II) on nano I-Sm in the aqueous solution was 256.41 ug/g

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일라이트(Illite)의 Physical Property

일라이트의 니켈(Ni) 흡착

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Exploring the Sorption Mechanism of Ni(II) on Illite: Batch Sorption, Modelling, EXAFS and Extraction Investigations

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The sorption mechanism of nickel (Ni) at the illite/water interface was investigated using batch, sorption modelling, extended X-ray absorption fine structure (EXAFS), and extraction approaches. The results showed that Ni(II) sorption on illite was strongly dependent on pH, contact time, temperature, and initial Ni(II) concentration. At a low initial Ni(II) concentration, the ion exchange species of $\equiv\text{X}_2\text{Ni}^+$ and the inner-sphere complexes including $\equiv\text{S}^-\text{ONi}^+$, $\equiv\text{S}^-\text{OHNi}^+$ and $\equiv\text{S}^-\text{ONiOH}^+$ species are observed on the sorption edges of Ni(II) on illite. As the initial Ni(II) concentration increased to 1.7×10^{-3} mol/L, precipitates including surface-induced precipitation of $\text{s-Ni}(\text{OH})_2$ and amorphous $\text{Ni}(\text{OH})_2$ became more significant, especially under neutral to alkaline conditions. EXAFS analysis confirmed that Ni-Al layered double hydroxide (LDH) can gradually form with an increase in the contact time. At pH 7.0, α - $\text{Ni}(\text{OH})_2$ was produced in the initial stage and then transformed to the more stable form of Ni-Al LDH with increasing contact time because of the increased Al^{3+} dissolution. With an increase in temperatures, α - $\text{Ni}(\text{OH})_2$ phase on illite transformed to Ni-Al LDH phase, indicating a lower thermodynamic stability compared to Ni-Al LDH phase. These results are important to understand the geochemical behaviors to effectively remediate soil contaminated with Ni(II).

Nickel (Ni) is one of the most toxic and widespread contaminants in the environment. There have been vast quantities of nickel released into the soil and water from industrial production such as mining, oil refining, electroplating, and battery and accumulator manufacturing^{1,2}. Once released into the environment, nickel readily transports and migrates as a soluble form of Ni^{2+} or Ni(II)-ligand complexes, which are very important and directly related to Ni(II) toxicity in environmental media. Therefore, Ni(II) can be easily assimilated by terrestrial and aquatic organisms and can gradually accumulate in the biological food chain. Although trace nickel is one of the essential elements for many organisms, a high level of Ni(II) is toxic and can cause cancer, nausea, vomiting, diarrhea, skin dermatitis, renal edema, and pulmonary fibrosis³⁻⁵. Therefore, the study of Ni(II) speciation and bioavailability at a solid/water interface is important for the prediction and evaluation of its ecological and environmental risks and toxicity and to the remediation of Ni(II)-contaminated soil and water.

Generally, the migration and retention of Ni(II) in contaminated soil and groundwater is largely controlled by its sorption and desorption behaviors at the solid/water interface. Previous studies have demonstrated that Ni(II) strongly and selectively interacted with phyllosilicate minerals that were widely distributed in the soil and sediments, such as montmorillonite⁶⁻¹⁰, kaolinite^{11,12}, bentonite^{13,14}, attapulgite^{15,16}, diatomite¹⁷, and illite^{18,19}. These studies showed that environmental factors such as pH, ionic strength, and temperature can affect the sorption/desorption behaviors of Ni(II) to a large extent at both the micro- and macro-scales. Moreover, ion exchange (IE) or the outer-sphere complexes (OSCs) were the primary mechanisms of Ni(II) sorption on clay minerals at a low

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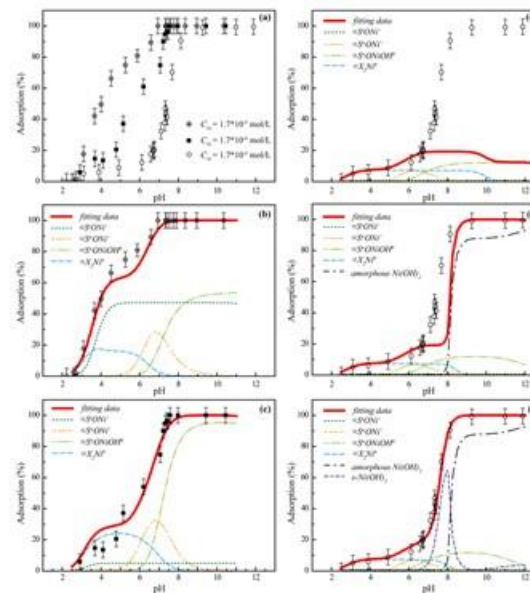


Figure 3. Sorption and modelling of Ni(II) on illite as a function of pH at different initial Ni(II) concentrations. (a) Sorption edges on illite at different initial Ni(II) concentrations. (b) Sorption model at $C_{0,\text{Ni(II)}} = 1.7 \times 10^{-3}$ mol/L. (c) Sorption model at $C_{0,\text{Ni(II)}} = 1.7 \times 10^{-4}$ mol/L. (d-f) Sorption model of cases 1, 2, and 3 at $C_{0,\text{Ni(II)}} = 1.7 \times 10^{-5}$ mol/L, $\text{S/L} = 2.0$ g/L, $I = 0.01$ M NaClO₄. All samples were tightly capped in centrifuge tubes and shaken for 1 week.

EXAFS spectra in this study, were formed and were possibly dominant for Ni(II) retention in the neutral to high pH range^{21,24-26}. Figure 3f shows that five different species were necessary to describe the sorption edge of Ni(II) on illite at $C_{0,\text{Ni(II)}} = 1.7 \times 10^{-5}$ mol/L. Below pH 6.5, the two species $\equiv\text{X}_2\text{Ni}^+$ and $\equiv\text{S}^-\text{ONi}^+$ were predominant, and the sorption were ~30% and 20%, respectively. In the pH range from 7.0 to 9.0, α - $\text{Ni}(\text{OH})_2$, amorphous $\text{Ni}(\text{OH})_2$, and the ISCs of $\equiv\text{S}^-\text{ONiOH}^+$ were responsible for Ni(II) sorption. Above pH 9.0, the ISCs of $\equiv\text{S}^-\text{ONiOH}^+$ and amorphous $\text{Ni}(\text{OH})_2$ were predominant. The sorption species and precipitates of Ni(II) at the illite/water interface were confirmed in the observed pH range by X-ray photoelectron spectroscopy in the supplemental information (SI).

EXAFS analysis of reference samples. EXAFS spectra and the radial structure functions (RSFs) of reference samples $\text{Ni}(\text{NO}_3)_2$, Ni-phyllosilicate, Ni-Al LDH, and γ - $\text{Ni}(\text{OH})_2$ are shown in Fig. 4. Figure 4a shows a monotonous feature of $\text{Ni}(\text{NO}_3)_2$ in the $k^2(k)$ function at $k > 3.0 \text{ \AA}^{-1}$, indicating that $\text{Ni}(\text{NO}_3)_2$ possessed a single coordination environment surrounding the Ni atoms that was primarily the hydration shell. The $k^2(k)$ functions of Ni-phyllosilicate, Ni-Al LDH and γ - $\text{Ni}(\text{OH})_2$ have more complicated oscillation features. At 5.0 \AA^{-1} , there was a small beat in the $k^2(k)$ function; notably, there was a typical split in the k -range of $\sim 7.5 \text{ \AA}^{-1}$, which is characteristic of Ni precipitation and is due to the neighboring atoms. Therefore, the sorption speciation was accurately distinguished from these characteristic oscillations in the $k^2(k)$ functions. Figure 4b shows the corresponding

중금속; 니켈(Ni)
흡착

Key Phrase

Ni(II) sorption on illite was clearly affected by the pH values. However, over 90% of the Ni(II) was adsorbed on illite above pH 8.0.

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일라이트(Illite)의 쓰임

한국광물학회지 (광물과산업) 제16권 제1호, 1-16, 2003
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논문

일라이트-운모의 이용 현황과 응용광물학적 특성 평가

조현구 · 노진환

경상대학교 지구환경과학과
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요약

수천 년 전부터 인간생활에 이용되어온 일라이트-운모는 다른 광물자원에 비하여 사용량은 많지 않지만, 요업, 도료, 종이, 건축용 재료, 확장용 소재 및 전자부품과 전기 재료 등 여러 산업 분야에 널리 사용되고 있다. 일라이트-운모는 광물학적으로 같은 계열의 광물군임에도 불구하고 산출상태, 입도 및 용도의 차이에 따라 다른 광물자원으로 취급되고 있다. 특히 국내에서 일라이트는 용어상의 혼란과 불명확한 법정 등록종류 때문에 효율적인 자원관리와 연구개발이 곤란한 실정이다. 그러므로 일라이트를 비롯한 점토광물 자원에 대한 광업법규상의 개선과 제도적 정비도 시급히 요구된다. 국내에서 개발되고 있는 일라이트-운모의 광석 유형은 그 광물상과 산출상태에 따라 페그마타이트상 백운모, 운모편암상 백운모, 납석상 일라이트 및 점토상 일라이트로 구분된다. 일라이트와 운모는 서로 다른 용도로 사용되고, 그 용도에 따라 그 품위 및 품질 개념이 다르다. 일라이트-운모 광석의 품위 및 품질 면에서 가장 기본적인 평가방식은 (1) 육안 및 편광현미경 관찰, (2) X-선회절 분석 및 (3) 화학분석인 것으로 생각된다. 특히 리트베틀법을 응용한 X-선회절 정량분석법은 일라이트의 품위를 산정하는데 유효한 수단이 될 수 있을 것으로 여겨진다. 국내 일라이트-운모 자원의 자원관리와 부가가치를 향상시키기 위해서는 광석에 대한 정확한 품위 평가로 가장 적절한 이용 분야를 모색해야 할 것으로 판단된다.

서언

16세기의 유명한 지질학자 아그리콜라(G. Agricola)에 의하여 '밋남' 또는 '반짝거림'을 뜻하는 라틴어 'micare'로부터 그 이름이 명명된 운모(Davis, 1985)는 오래전부터 인류에 의하여 이용된 광물질 중의 하나이다. 인도 신화에서 구름과 천국을 의미하는 'abracadabra' (힌두어로 'Abrak and Abhra')로 인용되는 운모는 신비한 의학품으로 이용되었다(Rajgarhia, 1951). 로마의 박물학자 플리니(Pliny the Elder)는 로마제국 대원형 경기장

(Circus Maximus)의 중앙에 위치했던 투기장의 바닥도포재(floor covering)로써 운모를 이용했다고 기록하고 있다. 14세기 에팔레치아 산맥 남부에 살던 아메리카 원주민들은 무덤의 장식품으로 이용하였으며, 러시아에서는 난로의 창과 개방된 불꽃등불의 것으로 이용하였다.

그러나 운모가 가지고 있는 독특한 성질 즉, 전기적 성질과 절연성이 본격적으로 이용되게 된 계기는 19세기 후반에 발명된 전기제품의 덕택이다. 특히 1904년 플레밍(John A. Fleming)의 진공관의 발명은 운모의 이용을 크게 증진시키는 계기가 되어, 운모는 절연제품,

다른 점토광물에 비하여 안정한 광물학적 특성 때문에 특정폐기물처분 시설에의 용용이 가능하며, 그런 연유로 인하여 일라이트 자체의 흡착 특성은 여전히 주목의 대상이다(추창오, 2001). 일라이트는 층간에 K^+ 를 함유하기 때문에 세슘(Cs)과 같은 $+1$ 가 방사성 양이온과 치환이 일어날 수 있으므로 환경방사능 연구에 매우 중요한 대상이다. 또한 일라이트의 Ca, Na, Ba, NH_4 등과 같은 다른 이온과의 흡착경쟁성, 및 유해중금속의 종류에 따른 흡착선택성 연구, 풍화작용과 용해반응, 층간양이온의 탈착 등은 많은 학자들에 의하여 연구되고 있는 중요한 대상이다.

최근 일라이트를 이용한 기능성 섬유들이 개발되어 기대를 모으고 있다. 이런 제품으로 일라이트론(illitlon)이 있다. 일라이트론은 미분쇄 일라이트 분말을 나일론, 폴리에스테르, 폴리프로필렌, 아크릴 등 화학섬유에 혼합시켜 상품화한 신소재이다. 이들은 축열, 탈취, 항균작용 등 고기능성 고부가가치 차세대섬유로 부상하고 있으며, 스포츠와 골프웨어에 주로 쓰인다.

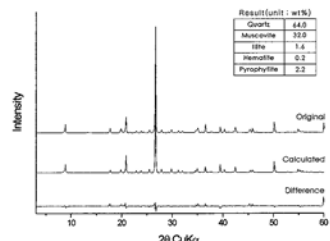


Fig. 1. Quantitative XRD results for the illitic pyrophyllite from the Bobae Mine.

국내산 일라이트-운모의 광물조성 및 응용광물학적 특성

일라이트 광석은 광물조성상 일종의 혼합물이기 때문에, 금속광물의 경우처럼 특정한 원소의 함량을 기준으로 품위를 산정하는 것은 불합리하다. 물론 일라이트나 백운모에 농집되는 K의 함량은 이 광물들의 함유 정도를 간접적으로 지시하기는 하지만, 이들에 대한 정량적 기준치는 될 수 없을 것으로 여겨진다. 통상 석영 등과 함께 미립질을 이루는 일라이트를 현미경 하에서 정량하는 것은 원칙적으로 불가능한 상황이다. 따라서 여기에는 최근에 개발된 X-선회절 정량분석법(quantitative phase analysis: QPA)이 적용되어야 할 것으로 여겨진다. 이 정량분석법은 원래 분말X-선회절 자료를 사용하여 광물의 구조를 검증하기 위해서 고안된 구조해석법(Rietveld, 1969)을 응용하여 개발된 것으로, 최근에 보다 개선된 형태의 상용 프로그램(SIEROQUANTTM, version 2.5)의 등장과 더불어 광물의 정량에 효과적으로 적용되기에 이르렀다(Taylor, 1991; Taylor and Matulis, 1994; Taylor and Hinczak, 2001). 실제로 이 분석법을 국내산 일라이트 광석(보배 광산의 도석질 일라이트 광석)의 품위 산정에 적용하여 비교적 재현성 있고 신뢰할만한 결과를 구할 수 있었다(Fig. 1).

국내에서 일라이트-운모는 흔히 산출되지만, 개발 대상이 될 정도로 고품위의 대규모 광산을 이루는 경우는 많지 않은 실정이다. 특히 대부분의 운모 광산은 경제성이 낮아 현재 휴광 내지는 폐광 상태에 있다. 휴광중인 3개소의 운모 광산에서 페그마타이트(지압광산, 가곡광산)와 운모편암(풍원광산) 상으로 산출되는 백운모 광석을 편광현미경 관찰 및 화학분석을 시행하였다. 대부분 암회색 내지 담회색을 띠는 운모편

실생활에 쓰이는 이유

층간 K^+ 를 함유 : 세슘 흡착

Key Phrase

세슘과 같은 $+1$ 가 방사성 양이온과 치환이 일어날 수 있으므로 환경방사능 연구에 매우 중요

화학섬유에 혼합시켜 축열, 탈취, 항균작용으로 스포츠와 골프웨어에 주로 쓰인다

일라이트(Illite)의 쓰임



Applied Clay Science 21 (2002) 155–163



Clay minerals and their beneficial effects upon human health. A review

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Abstract

This work examines the **beneficial effects for human health of clay minerals**, describing their use in pharmaceutical formulations, spas and aesthetic medicine. Their therapeutic action as active principles in pharmaceutical formulations orally administered (gastrointestinal protectors, laxatives, antidiarrhoeics) or for topical applications (dermatological protectors and cosmetics) is described. Their use as excipients and their influence in the bioavailability of the organic active principle is also described, both in the liberation process and in its possible degradation effect. Among their uses in spas, clay minerals therapeutic activity, in geotherapy, pelotherapy and paramuds is commented upon. Moreover, **the applications of the clay minerals in aesthetic medicine (to clean and moisturise the skin and to combat compact lipodystrophies, acne and cellulite) are also described**. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Clay minerals; Pharmaceutical formulations; Spas; Aesthetic medicine

1. Introduction

The use of minerals for medicinal purposes is almost as old as mankind itself. Minerals have been used for curative ends since Prehistory. There are indications that *Homo Erectus* and *H. Neanderthalensis* used oclres mixed with water and different types of muds in order to cure wounds, soothe irritations, as a method of cleansing the skin, etc. This might have been due to their mimicking animals, many of which instinctively use minerals for the above purposes. The use of medicinal earths in Mesopotamia and Ancient Egypt has also been proven. The use of Nubian earth as an anti-inflammatory or the use of mud materials for mummification of cadavers can be cited as exam-

ples (Bech, 1987; Robertson, 1996; Veniale, 1997). In the Ancient Greek period, mud materials (Lemnos Earth) were used as antiseptic cataplasms to cure skin afflictions, as cicatrizers or as a cure for snake bites. Both Hippocrates and Aristotle, among others, produced classifications of medicinal earths. Most of these materials are clays, given different names depending on their origins or on the differences in their mineralogical composition and properties. For example, *Terra Samia*, *T. Sigillata*, *T. Lemnia*, *T. Cimolia*, *T. Soudipica*, *T. Eretria*, *T. Negra*, etc. (Bech, 1996; Giammatteo et al., 1997). Furthermore, Cleopatra, Queen of Egypt, used muds from the Dead Sea for cosmetic purposes and Marco Polo describes how in his travels he saw Muslim pilgrims cure fevers by the ingestion of "pink earth" (Veniale, 1996).

The first written reference known to exist upon the use of "stones" and a description of their curative

bowel, its pH slowly rises and it forms an acid–base equilibrium, which will give rise to the neutral clindamycin form. As the drug is physically adsorbed in the clay by ionic forces, it is desorbed slowly in the bowel, where the majority of drugs are absorbed, when it changes into a neutral form. Therefore, the absorption of clindamycin is favoured when it is administered with montmorillonite and its therapeutic action is prolonged (Porubcan et al., 1978).

The beneficial effect of retarding the liberation of a drug united to a clay mineral can also be achieved by increasing the ionic force on coming into contact with the intestinal fluid, if administered orally, or with the skin if administered topically. Therefore, some minerals, such as talc and kaolinite, which are used as dermatological protectors and adsorbents, can carry superficially adsorbed antibiotic, analgesic or antihistaminic which are released on contact with damp skin.

Another example of the liberation advantages where an interaction exists between the drug and mineral is that of water-resistant sun screens. Sepiolite and smectites have the ability to form complexes with organic compounds which absorb ultra-violet radiation thus enabling them to be used in sun screens with protection factors (Del Hoyo et al., 1998; Vicente et al., 1989). Absorption/desorption studies carried out, have demonstrated that the level of absorption is good and that even systems containing low drug levels have a great ultraviolet radiation absorption capacity. The adsorption of *N*-methyl-8-hydroxy quinoline methyl sulphate on smectite makes the active principle's desorption in salt water slower, which means that the active principle remains on the skin longer during bathing (Vicente et al., 1989).

2.3.2. Influence in the drug's degradation

The phenomena of interaction between a drug and a mineral excipient can accelerate the drug's degradation, thus losing its therapeutic activity. This has been demonstrated in numerous research works carried out in recent years (Porubcan et al., 1979; Hermosin et al., 1981; Cornejo et al., 1983; Forteza et al., 1988, 1989). It has been proven, for example, that dexamethasone, an anti-inflammatory, degrades in the presence of palygorskite and sepiolite although this degradation is more rapid in the presence of the former, because of the Fe of palygorskite catalyses the degradation reaction. The same result has been

obtained for other anti-inflammatories such as hydrocortisone.

The degradation of a drug can occur in the presence of a clay mineral, even though the two are not administered in the same pharmaceutical formulation. The mineral's surface carries a negative charge, which means that while it is in the stomach it will absorb protons. If a drug which degrades in the presence of protons coincides in the stomach with a clay mineral, it will degrade more rapidly than if the mineral were not there. This is the case with digoxin, a cardiovascular tonic that degrades by hydrolysis, catalysed by acids, in the presence of montmorillonite. Studies undertaken have demonstrated that the drug degrades more rapidly in the presence of montmorillonite than when it is dissolved alone. At pH 2, digoxin degrades 20% in 1 h while in the presence of montmorillonite it degrades completely in the same time (the time of gastric residence), a fact to be taken into account when administering it (Porubcan et al., 1979).

3. The use of clay minerals in spas

Clay minerals are widely used in spas. They are mixed with water (geotherapy), mixed with sea or salt lake water, or minero-medicinal water, and then matured (pelotherapy) or mixed with paraffin (paramuds). **The clay minerals which are most used are smectites and kaolinite, although illite and palygorskite are also used.** They are applied alone or more frequently as complex clay minerals muds. Calcite, quartz, feldspars, etc., sometimes are present as minor or trace minerals. **The principal properties of these clay minerals which make them useful in spas are: their absorption/adsorption capacity, their high cation exchange capacity, plastic properties, rheological properties, grain size and cooling index** (Bettero et al., 1999; Cara et al., 1999, 2000a,b; Ferrand and Yvon, 1991; Gorgoni et al., 1999; Jobstraibizer, 1999; Minguzzi et al., 1999; Sánchez et al., 2000a; Summa and Tateo, 1998; Yvon and Ferrand, 1996; Veniale, 1997; Veniale and Setti, 1996).

On the other hand, it is necessary to study the presence of toxic elements as As, Pb, Hg, Cd, Se, Sb, Cu, Zn, etc., in the clay–water mixed used in spas, about all, it is necessary to know their mobility for avoid possible intoxications. It is important to know if

스파(Spa) 분야에서 주요
하게 쓰이는 이유

노폐물제거
(흡수, 흡착,
양이온교환능)

Key Phrase

The clay minerals which are most used in spas are smectites and kaolinite, although **illite** and palygorskite are also used.

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폴리프로필렌 부직포 섬유의 열, 항균 및 원적외선 방사 특성에 미치는 불소화 일라이트 첨가의 영향

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Influence of Fluorinated Illite on Thermal, Antibiotic and Far-infrared Emission Properties of Polypropylene Non-woven Fibers

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초록: 본 연구는 폴리프로필렌 수지에 불소화된 일라이트를 함량별로 첨가하여 제조한 일라이트/폴리프로필렌(PP) 부직포의 열적 특성, 항균성, 원적외선 방사율을 고찰하고자 하였다. 불소화 일라이트 첨가 폴리프로필렌 섬유의 열적 특성은 열중량 분석을 사용하여 조사하였다. 그 항균 특성은 황색포도상구균과 폐렴간균의 균주 실험으로, 원적외선 방사율은 푸리에 변환 적외분광법을 사용하여 알아보았다. 그 실험결과, 일라이트/PP 부직포 섬유의 열적 특성 및 항균성, 원적외선 방사율은 불소화 일라이트의 함량이 증가할수록 증가되었고, 특히 불소화 일라이트 5 wt% 함유 PP 부직포 섬유의 경우가 일라이트를 함유하지 않은 PP 부직포에 비해 각각 10.3, 41.2 및 9.8%로 크게 증가하였다. 이는 일라이트의 불소화로 인하여 고분자 사슬 사이의 계면결합력의 향상 때문이라 판단된다.

Abstract: In this work, the thermal, antibiotic properties and far-infrared emissivity of fluorinated illite embedded polypropylene non-woven fibers (f-illite/PP fibers) were investigated in the presence of 0, 1, 3, 5 and 7 wt% illite powders. The thermal properties of f-illite/PP fibers were studied by thermogravimetric analysis (TGA). Their antibiotic properties were examined by *Staphylococcus aureus* and *Klebsiella pneumoniae* test. Their far-infrared emissivity was also investigated by Fourier transform infrared spectroscopy. From the experimental results, thermal, antibiotic properties and far-infrared emissivity of f-illite/PP fibers were improved by increasing fluorinated illite contents and the property values of 5 wt% f-illite/PP fibers were increased remarkably by about 10.3, 41.2 and 9.8% respectively in comparison with PP non-woven fibers having no fluorinated illite additive. This result was interpreted as the development of interfacial adhesion force between the polymer chains due to the fluorination of illite powder.

Keywords: illite, polypropylene, fluorination, far-infrared emissivity, antibiotic property.

서 론

최근 친환경성 고분자 복합재료에 대한 관심이 커짐에 따라 천연 물질을 충전제로 활용하여 고분자 복합재료의 다양한 물성을 향상시키는 연구가 활발히 진행되고 있다.¹⁻⁴ 특히 천연 점토광물은 고분자에 충전제로 이용하였을 때, 복합재를 형성하여 난연성, 열 안정성, 기계적 강도 등의 다양한 고분자 물성을 크게 향상시키는 것으로 알려져 있다.⁵⁻⁸ 이러한

점토광물 중 최근 가장 많이 사용되고 있는 것으로는 몬토릴로나이트(montmorillonite, MMT)가 있다.⁹ MMT는 각 층의 길이가 약 218 nm, 두께가 약 1 nm, 각 층간 거리가 1 nm인 적층 구조를 가지고 있다. 또한 점토층의 종횡비(aspect ratio)가 200-2000 정도로 매우 커서 다른 충전제에 비해 매우 우수한 보강제로 작용한다.¹⁰⁻¹² 또한 일라이트(illite, K₂H₃O(AlMg₂Fe)(Si₄Al)₂O₁₀(OH)₂·H₂O)도 이와 같은 천연 점토광물이며, 실리온(Si)과 알루미늄(Al)이 주성분으로 구성되고, 한 층의 두께가 약 1 nm인 층상 구조를 가지고 있다. 특히 일라이트는 MMT보다 매질량이 더 풍부하며, MMT에 비하여 종횡비 값이 크기 때문에 고분자와 복합재를 제조시 다양한

폴리프로필렌 부직포 섬유의 열, 항균 및 원적외선 방사 특성에 미치는 불소화 일라이트 첨가의 영향

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적외선 방사성능에 영향을 미치는 것을 알 수 있으며, 일라이트/PP 부직포가 원적외선 방사 가능성 소재로 충분히 활용이 가능할 것으로 기대된다.

결 론

본 연구에서는 PP 수지에 불소화된 일라이트를 함량별로 첨가하여 제조한 일라이트/PP 부직포의 열적 특성, 항균성, 원적외선 방사 특성을 고찰하여 다음과 같은 결론을 얻었다. 머처리 일라이트는 섬유와 잘사며 인하여 부직포 제조가 가능한 반면, 불소화 일라이트/PP 부직포는 제조가 가능하였다. 불소화된 일라이트의 함량이 증가함에 따라 열적 특성, 항균성, 원적외선 방사율 등이 모두 증가하는 경향을 보여 주었다. 즉, 불소화 일라이트가 5 wt% 첨가된 PP 부직포는 순수 PP보다 열적 특성이 약 10% 향상되었고, 황색포도상구균 및 폐렴간균의 항균특성도 35.1, 47.3%가 향상되었다. 또한 불소화된 일라이트 5 wt%를 함유한 부직포는 96.5%의 원적외선 방사율과 3.98×10³ W/m²의 방사에너지를 가지며, 순수 PP 부직포보다 9.8% 향상되어 우수한 원적외선 방사 특성을 보여주었다. 이러한 불소화 일라이트 첨가 PP 부직포의 열적 특성, 항균성, 원적외선 방사 특성을 향상은 점토광물인 일라이트의 불소화로 인하여 고분자 사슬 사이의 계면결합력의 향상때문으로 여겨진다.

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원적외선 방출 및 항균/ 섬유에 이용

Key Phrase

일라이트/PP 부직포 섬유의 열적 특성 및 항균성, 원적외선 방사율은 불소화 일라이트의 함량이 증가할수록 증가, 특히 불소화 일라이트 5 wt% 함유 PP 부직포 섬유의 경우가 일라이트를 함유하지 않은 PP 부직포에 비해 각각 10.3, 41.2 및 9.8%로 크게 증가

Summary

A

원적외선 및 음
이온 방출/
항균, 탈취 (암모니아) 능

FIR 방출

4~1,000um 원적외선 파장 방출

- 식물 : 생육, 세포활성
- 유기물 : 항균

A

COD : 86%
BOD : 71.86%
유기물 저감
노폐물 감소

물리·화학적 흡착

다공질 및 물과의 수소결합

- 환경 : 오염수질의 거름효과, 생물학적
화학적 산소요구량 감소
- 피부 : 피부 노폐물 흡착

A

Pb, Ni, TI(I), CS
Heavy Metal
흡착/소거

양이온 교환에 따른 중금속 제거

탁월한 흡착/소거 기능