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Effect of Structure on the Sorption Properties of Chlorine-containing Form of Double Aluminum Lithium Hydroxide

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Abstract—The effect exerted by composition and specific structural properties of commercial batches of granular sorbent based on chlorine-containing form of double aluminum lithium hydroxide on its sorption properties in lithium extraction from magnesium chloride brines was determined. Deficiency in lithium chloride in the sorbent structure and structural defects are responsible for the selectivity of granular sorbent. It was shown that sorbent is selective for lithium even in the presence of high concentrations of magnesium chloride in brine and the borate ions exhibit adverse effect on the technological process.

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Several methods exist for producing chlorine-containing form of double aluminum lithium hydroxide, LiCl·2Al(OH)\textsubscript{3}·\textit{m}H\textsubscript{2}O (DGAL-Cl), by intercalation of lithium chloride into Al(OH)\textsubscript{3} layered structure. It was shown \cite{1, 2} that sorption properties of DGAL-Cl depend on preparation conditions.

The study of DGAL-Cl formation from crystalline aluminum hydroxide (gibbsite) showed that intercalation of LiCl into Al(OH)\textsubscript{3} layered structure precedes disordering of Al–OH layers in the areas where Al(OH)\textsubscript{3} and LiCl phases are in contact \cite{3–5}. The intercalation process intensifies when Al(OH)\textsubscript{3} is in the form of defect matrix obtained by chemical or mechanochemical method \cite{1, 3}. In this case, a compound obtained has defect structure of the initial compound. This compound is suitable for reversible intercalation of LiCl from salt media (sorption) and its deintercalation (desorption) in subsequent treatment with water. This property of DGAL-Cl and presence of structural defects were used for preparing reversible sorbents for selective removal of lithium from multicomponent salt systems \cite{2, 4}.

Efficient methods are available for the preparation and granulation of DGAL-Cl with structural defects \cite{6–9}. These methods were used to develop industrial sorbent technology and equipment for sorption treatment of multicomponent natural brine to remove lithium \cite{10–12}. Along with this, the behavior of other cations, especially of Mg\textsuperscript{2+} whose ionic radius is close to Li\textsuperscript{+}, present in the brine and their effect on its enrichment in lithium was determined. It made it possible to eliminate the arising hypotheses about the possibility of Mg\textsuperscript{2+} intercalation into DGAL-Cl containing structural defects.

In the study, the composition and structure of industrial granular sorbent were determined and the properties of the DGAL-Cl granular sorbent containing structural defects were studied in selective removal of lithium chloride in the form of its aqueous solution from natural lithium-bearing magnesium chloride brines under industrial conditions.
EXPERIMENTAL

Air-dry samples of the sorbent batches were dissolved in nitric acid and their chemical composition was determined.

Aluminium and magnesium in the compound and brine were determined by complexometric methods [13] and Cl and B ions, by titration with mercury nitrate and mannite, respectively [14]. Lithium was determined on an AAS-1 atomic absorption spectrometer. The X-ray phase analysis was performed on a DRON-3 diffractometer (Cu Kα radiation) and the pH was measured on an OP-208 precision digital pH-meter.

The crystal optics analysis of the crystalline and defect-containing DGAL-Cl samples was carried out on a POLAM-L-211 polarization microscope in immersion liquids. The crystal optics analysis [15] was combined with the X-ray analysis [16]. Electron microscopic examination was performed on a TM-1000 scanning electron microscope equipped with the energy dispersive spectral attachment. The specific surface area was determined by mercury porosimetry.

Preparation of DGAL-Cl with structural defects and its composition. DGAL-Cl powder was produced in industry by chemical precipitation from the aluminium-lithium system AlCl₃–LiOH–H₂O [6, 7] by reaction

\[ 2\text{AlCl}_3 + 6\text{LiOH} + m\text{H}_2\text{O} = \text{LiCl·2Al(OH)₃·mH}_2\text{O} + 5\text{LiCl}. \]  

Owing to structural defects, DGAL-Cl formed by chemical precipitation from aluminum-lithium system by the method [7] has the composition and physical characteristics, which differ from corresponding characteristics of crystalline samples obtained under equilibrium conditions [4, 5]. DGAL-Cl and granulated sorbent on its basis were obtained on an industrial complex for producing lithium carbonate from LiCl-enriched lithium concentrates in China (Qinghai). Their composition is given in Table 1. As raw materials were used magnesium chloride lake brines.

The DGAL-Cl powder obtained in different volumes and at different times has the stable composition: the Li:Al atomic ratio (at. rat.) is 0.38 ± 0.01 and the average content of Li in it, 20.7 mg Li/g⁻¹ of the sorbent (see Table 1).

Owing to favorable rheological properties, the DGAL-Cl precipitates formed under the above conditions can be easily granulated. As binder for granulation we used chlorinated polyvinyl chloride resin (CPVC) of the chinese production, which is soluble in organic solvent, methylene chloride [8, 9]. After removal of methylene chloride, the resulting granulated sorbent contains 90–92% DGAL-Cl. We used 1-2 mm fraction obtained from classification of the material. Its mechanical resistance to abrasion in liquids, determined under the standard conditions, exceeds 98% [4, 8].

The LiCl content in the granular sorbent corresponds to 11 ± 0.7 wt%, or 19 ± 0.5 mg Li/g⁻¹ of the sorbent. From the sorbent, up to 40% lithium chloride can be deintercalated with fresh water to ensure lithium-deficient composition. Lithium deficiency is reduced in the course of lithium sorption from brine and is its theoretical sorption capacity [4].

The DGAL-Cl formed under equilibrium conditions or by intercalation of LiCl into crystalline Al(OH)₃ has the Li:Al atomic ratio equal 0.5, and no more than 10% lithium may be deintercalated from it without distortion of DGAL-Cl crystalline structure (Table 1 for comparison).

Enlarged and commercial batches of granular sorbent were obtained and charged into the sorption-desorption columns, with sorbent volume varied from 8 to 28 tons. For lithium enrichment on granular sorbent we used lithium-bearing lake brine containing (g l⁻¹): LiCl 4.85, MgCl₂ 424, NaCl 5.15, CaCl₂ 1.2, SO₄²⁻ 3.4, and B₄O₇²⁻ 2.35 (or 0.66 in terms of B). Brine pH was 5.4. In a

<table>
<thead>
<tr>
<th>Conditions of Synthesis and Place</th>
<th>DGAL-Cl powder</th>
<th>Granular DGAL-Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LiCl</td>
<td>Al(OH)₃</td>
</tr>
<tr>
<td>Lab-enlarged (Russia)</td>
<td>12.8</td>
<td>61.5</td>
</tr>
<tr>
<td>Pilot plant (China, 2010)</td>
<td>12.7</td>
<td>61.5</td>
</tr>
<tr>
<td>Industrial (China, 2012)</td>
<td>12.1*</td>
<td>57.6</td>
</tr>
</tbody>
</table>

* The average value of several batches