PhD Thesis

Formation and Neutralization of Some Reactive Components Relevant to Bayer Alumina Production and Their Application as Adsorbents

Eszter Kása

SUPERVISOR:
Prof. Dr. Pál Sipos

UNIVERSITY OF SZEGED

Doctoral School of Chemistry
Department of Molecular and Analytical Chemistry
Faculty of Science and Informatics

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1. Introduction and aims

In the aluminum industry, aluminum oxide is typically produced from bauxite using the Bayer process, followed by the production of pure aluminum through the Hall-Héroult electrolysis process. A well-known by-product of the Bayer process is red mud, which, due to its high pH and large volume, has led to numerous environmental disasters worldwide. Although both industry and academia are making serious efforts to mitigate the red mud issue, no global, universally accepted solution has been found yet. My work focuses on understanding the processes involved in the Bayer process and exploring the potential of the by-products.

In the first part of my doctoral thesis, I investigated the dissolution kinetics of kaolinites prepared in various ways - untreated, mechanochemically processed, and through thermal treatment - in sodium aluminate solution, which corresponds to the composition used in the industrial Bayer process. Since kaolinite is a vital component of bauxite, its physical and chemical properties are crucial from an industrial perspective. A key factor is the concentration of dissolved silicon over time, which depends on the dissolution rate of kaolinite and the formation of sodalite. For instance, mechanochemical treatment can positively influence reaction kinetics by increasing the reactive surface area and the number of active (acidic) sites, thereby enhancing interactions among aluminum, silicon ions, and hydroxide ions, and accelerating the dissolution process. My experimental results indicated that the primary drivers of physical and chemical transformations include particle fragmentation, delamination, and structural defects associated with amorphization. Additionally, the dehydroxylation of Al/Si−OH groups contributed significantly to these changes.

The properties of sodalite were greatly affected by the nature of the starting kaolinite and the composition of the impurities present in the aluminate solution. I synthesized sodalite in the presence of organic impurities and examined its adsorption capacity regarding the Basic Violet 14 (BV14) dye molecule. While I did not observe significant differences between their crystal structure, morphology, and elemental composition, their specific surface areas varied considerably. This variation indicated a strong correlation with the total amount of organic contaminants, whether attached to the sodalite surface or located within its pores. Nonetheless, the tests did not reveal a clear relationship between the organic contaminants present during sodalite formation and the amount of dye adsorbed. When comparing the adsorption capacity of sodalite with that of a zeolite designed for the same purpose, I found that sodalite can bind up to three to four times more BV14, despite having a much smaller specific surface area. This suggests that adsorption capacity is not solely related to specific surface area but is likely influenced more by the size compatibility of dye molecules and the pore structure.

In the final section of my dissertation, I investigated the production of high purity tricalcium aluminate hydrate (TCA) under conditions typical of aluminum industry technologies. I compared the TCA produced using a new synthetic process with a sample created using a conventional method, which was a reference. I found no significant differences in their physical and chemical properties, and their solubility remained identical in both distilled water and a 1 M NaCl solution. Additionally, I studied the reaction mechanism between 1 M HCl and TCA and proposed a new mechanism that has not been published previously in the literature. According to the findings, hydrocalumite (LDH) forms after the dissolution of TCA, with its amount increasing with the acid concentration. However, at neutral pH (pH = 7), only aluminum hydroxide appears as a solid phase.

The primary goal of my doctoral work was to gain a deeper understanding of the processes occurring under industrial conditions, with a focus on kaolinite dissolution and sodalite formation. I aimed to identify the relationship between the properties of sodalite and the dissolution processes to control these processes within the industry, thereby accelerating and enhancing the efficiency of the Bayer process. Simultaneously, I sought to explore the potential of the sodalite generated through this process. I believe that this portion of my work could lay the groundwork for numerous studies on adsorption in various flow-through reactors, while also addressing larger industrial scales.

The neutralization of red mud, which forms the last part of my thesis, turned out to be an enormous task that exceeds the scope of doctoral work. Fortunately, several members of my research group are working on it in various forms, and I hope that my research on the neutralization of tricalcium aluminate hexahydrate (TCA) will contribute to a comprehensive solution.

2. Experimental

The basis for the syntheses was a sodium aluminate solution prepared by me. As a first step, I prepared a carbonate-free, supersaturated sodium hydroxide solution. To do this, I dissolved NaOH flakes in distilled water and then filtered the resulting Na_2CO_3 precipitate through a PTFE membrane. Finally, I standardized it with HCl solution by simple acid-base titration.

Next, the sodium aluminate solution was prepared by slowly dissolving aluminium shots into a diluted (9 M) NaOH solution, keeping the whole system carbonate-free by using a reflux equipped with a CO_2 pipe. The aluminium was slowly added to the mixture; the whole process took 4-5 days, then it was filtered, and the exact concentration of the sodium aluminate solution was determined by classical titration. The final concentrations of the solution used for the sodalite preparation were 2.6 M of NaOH and 1.9 M of $[AlOH_4]^-$, fitting the concentration of the spent liquor in the industry. On the other hand, for the tricalcium aluminate hexahydrate synthesis, the so-called pregnant or green liquor (with the concentrations of 3.4 M NaOH and 4.6 M $[AlOH_4]^-$) was prepared with the same method.

Sodalites were the products of the dissolution experiments, carried out in a closed PTFE vessel specifically designed and implemented for this purpose. The spent liquor was stirred and heated up to 95 ± 0.5°C in this vessel by using a silicon oil bath. First, sodium sulfate (0.05 M) and sodium carbonate (0.2 M) were dissolved in the liquor, then 0.09 M kaolinite was dosed gradually into the vessel. In some cases, organic compounds were also added to the mixture to mimic the industrial impurities. After six hours of stirring, the dispersion was filtered through a 0.45 μm PTFE filter, and the solid was dried at 60°C, in air.

For the synthesis of the tricalcium aluminate hexahydrate (TCA), calcium oxide (obtained by the calcination of calcium hydroxide at 1000°C for 8 hours) was added to the green liquor (Ca:Al molar ratio was 1:1), in the same apparatus as the one used during the sodalite synthesis. After mixing the starting materials at 95°C for four hours, the dispersion was filtered, washed with distilled water, and dried under N_2 atmosphere. The TCA prepared with this method hereafter will be named Bayer TCA. Another method was also used for TCA synthesis, and its product will be called reference TCA. Here, calcium oxide (obtained from the calcination of calcium carbonate at 1000°C for 12 hours) and aluminium oxide ($CaO:Al_2O_3 = 3:1$ molar ratio) were calcined at 1300°C. Then the oxide was hydrated for two days at 95°C, washed with distilled water, and dried under N_2 atmosphere. This method was found in the literature and was only used as a reference in this study.

To characterize the solid materials I produced, I used several testing methods, and in some cases, we used (since I was unable to measure everything personally with all the instruments):

- Powder X-ray diffraction (XRD) patterns of the solids were recorded on a Rigaku Miniflex II instrument.
- The morphologies of the materials were examined by scanning electron microscopy (SEM, Hitachi S–4700 type II). The microscope was also equipped with an energy dispersive X-ray analysis detector (Röntec QX2 spectrometer with Be window).
- The solids were investigated by Fourier-transform infrared spectroscopy, FT–IR (BIO-RAD Digilab Division FTS-65A/896FT-IR spectrophotometer).
- The water and organic compound content of the samples was probed by thermogravimetric analysis using a TA Instruments Discovery TGA instrument coupled with a mass spectrometer (MS, Hiden Analytical, HPR-20 EGA).
- The specific surface area and acidity of the samples were mapped by a BELCAT-A catalyst analyser. The NH3 desorption was detected by a thermal conductivity detector (TCD).
- The total organic carbon (TOC) content of the solids was measured with an Analytik Jena N/C® 3100 apparatus equipped with an NDIR detector.
- A Malvern NanoZS dynamic light scattering (DLS) instrument operating with a 4-mW helium-neon laser light source was applied to map the heterogeneity in the particle diameters in solution (due to various degrees of aggregation) and hydrodynamic diameters of the materials at room temperature.
- The point of zero charge (PZC) of the solids was also determined with the pH drift method, where the pH of the suspensions was measured with a SenTix H glass electrode.

ICP-OES with radial configuration (Thermo Scientific iCAP 7400 ICP-OES DUO spectrometer) was used for the determination of the chemical composition of the kaolinite samples and silica concentration in the Bayer liquor samples. The concentration of the remained dye was determined at λmax = 564 nm with an Analytik Jena Specord 210 Plus double beam UV-Vis spectrophotometer, using a standard quartz cuvette with 1 cm optical length. Potentiometric titrations were performed using a titroprocessor (Metrohm 888 Titrando using tiamo™ 2.5 software for titration control, Metrohm AG, Switzerland) employing an InLab Expert Pro-ISM combined pH electrode from Mettler Toledo.

3. New scientific results

T1. We demonstrated that the dissolution kinetics of kaolinite samples of different origins under Bayer process conditions are governed by the combined effects of multiple physical and chemical parameters. Among these, the specific surface area, total pore volume, aggregation state of primary particles, and the number of Lewis acidic surface sites exert the most significant influence on the dissolution process.

The dissolution kinetics cannot be attributed to a single property of kaolinite; the process can only be fine-tuned by altering several parameters. Specifically, a larger specific surface area and greater total pore volume accelerate dissolution, only if the number of Lewis acidic surface sites does not decrease significantly the process.

T2. We were the first to show that the presence of a new phase generated by grinding accelerates the dissolution of kaolinite. Pre-treatments induce similar changes in the physicochemical properties of kaolinite samples with initially different characteristics, which leads to convergence in their dissolution kinetics.

Based on our findings, the formation of amorphous metakaolinite accelerates dissolution and homogenizes the sodalite formation process. Amorphization of the crystal structure, delamination, and dehydration of the particles not only speed up the reaction but also increase the amount of dissolved Si(IV) in the aluminate solution, regardless of the initial properties of the kaolinite. Furthermore, we established that the sequence of pretreatments - namely, grinding and thermal treatment - is of critical importance in determining the dissolution kinetics of kaolinite. The amount of dissolved silicon can be further increased if the sample is first ground and then calcined.

T3. We established that kaolinite samples delaminated and fragmented by grinding exhibit rapid, quasi-instantaneous dissolution under industrial alumina production conditions. Dehydroxylation enhances the amount of silicon dissolved. We successfully intercalated dimethyl sulfoxide between the kaolinite layers and demonstrated that the weakening of hydrogen bonds facilitated delamination and the dissolution process.

To map the factors influencing kaolinite dissolution, we successfully intercalated dimethyl sulfoxide between the layers. The intercalation had a similar effect to calcination: it facilitated the delamination process during dissolution by weakening the hydrogen bonds that connect the layers.

T4. We experimentally confirmed that the sodalite synthesized in our study exhibits a higher adsorption capacity for the dye molecule Basic Violet 14 than the reference zeolite. The enhanced efficiency is attributed to the greater number of hydroxyl(ate) groups present on the surface of the sodalite, which interact with the protonated amino groups of the dye molecule.

Both adsorbents, both sodalite and zeolite, possess surface hydroxyl(ate) groups, which bind dye molecules via electrostatic attraction and hydrogen bonding at pH values above the point of zero charge (PZC). Theoretical calculations suggest that the sodalite surface contains a significantly higher number of binding sites, which likely accounts for its superior performance as an adsorbent for Basic Violet 14. In the case of this relatively large dye molecule, the higher specific surface area of the zeolite does not contribute effectively, as the adsorbate is unable to penetrate the pores.

T5. We confirmed that the presence of organic components (e.g., carboxylic acids) during sodalite synthesis can influence the adsorption properties of the final product. In certain cases, the surface-bound carboxylate groups enhance adsorption efficiency.

According to total organic carbon (TOC) measurements, organic compounds remained incorporated in the sodalite structure. Further characterization methods revealed a reduction in the specific surface area of the samples, which did not impact negatively the adsorption performance. On the contrary, in some cases, surface-bound carboxylate groups had a positive effect on sorption. For instance, the SOD-NaPAC sample adsorbed 40 mg/g more dye than sodalite synthesized without any organic additive.

T6. We investigated the reaction mechanism between hydrated tricalcium aluminate and hydrochloric acid. We were the first to demonstrate that at pH ≈ 11, layered double hydroxide (hydrocalomite) is formed, which is converted to metal chloride under the influence of hydrochloric acid. We found that in an acidic medium, increasing the concentration of sodium chloride accelerates the formation of the solubility equilibrium of aluminum hydroxide.

Based on the reaction mechanism proposed by us, TCA first converts to layered double hydroxide before completely converting to $Al(OH)_3$. We observed that, regardless of the synthesis method, 6 equivalents of acid are required for the complete neutralization of TCA. The reaction medium plays a crucial role in the mechanism; increasing the concentration of NaCl in an acidic solution significantly reduces the time required to reach equilibrium.

4. Publication list

Hungarian Scientific Bibliography (MTMT) identifier: 10069343
h-index: 5

Original research articles related to the PhD dissertation:

1. **Eszter Kása**, Ivett Petri, Márton Szabados, Áron Ágoston, András Sápi, Zoltán Kónya, Ákos Kukovecz, András Stirling, Pál Sipos, Bence Kutus, *Utilization of desilication products as efficient adsorbents for the removal of basic fuchsine.* Journal Of Hazardous Materials, 480 (2024) 136234. https://doi.org/10.1016/j.jhazmat.2024.136234. D1, IF_{2024}: 11.3; number of independent citations: 2.
2. **Eszter Kása**, Yvette Szabó, Márton Szabados, Zsolt Kása, Zoltán Kónya, Ákos Kukovecz, Pál Sipos, Bence Kutus, *The neutralization of tricalcium aluminate hexahydrate and its spontaneous transformation into Friedel's salt, a layered double hydroxide*. Cement And Concrete Research, 177 (2024) 107414. https://doi.org/10.1016/j.cemconres.2023.107414. D1, IF_{2024}: 13.1; number of independent citations: 5.
3. **Eszter Kása**, Kornélia Baán, Zsolt Kása, Zoltán Kónya, Ákos Kukovecz, István Pálinkó, Pál Sipos, Márton Szabados, *The effect of mechanical and thermal treatments on the dissolution kinetics of kaolinite in alkaline sodium aluminate solution under conditions typical to Bayer desilication.* Applied Clay Science, 229 (2022) 106671. https://doi.org/10.1016/j.clay.2022.106671. Q1, IF_{2024}: 5.8; number of independent citations: 5.
4. **Eszter Kása**, Márton Szabados, Kornélia Baán, Zoltán Kónya, Ákos Kukovecz, Bence Kutus, István Pálinkó, Pál Sipos, *The dissolution kinetics of raw and mechanochemically treated kaolinites in industrial spent liquor – The effect of the physico-chemical properties of the solids*. Applied Clay Science, 203 (2021) 105994. https://doi.org/10.1016/j.clay.2021.105994. Q1, IF_{2024}: 5.8; number of independent citations: 9.

Related research ΣIF=36.0

Publications not directly related to the PhD dissertation:

1. Zsolt Kása, Enikő Bárdos, **Eszter Kása**, Tamás Gyulavári, Lucian Baia, Zsolt Pap, Klara Hernadi, *Myth or reality? A disquisition concerning the photostability of bismuth-based photocatalysts.* Journal of Environmental Chemical Engineering, 10 (2022) 107624. https://doi.org/10.1016/j.jece.2022.107624. Q1, IF_{2024}: 7.2; number of independent citations: 3.
2. Zsolt Kása, **Eszter Orbán**, Zsolt Pap, Imre Ábrahám, Klára Magyari, Seema Garg, Klara Hernadi, *Innovative and Cost-Efficient BiOI Immobilization Technique on Ceramic Paper—Total Coverage and High Photocatalytic Activity*. Nanomaterials, 10 (2020) 1959. https://doi.org/10.3390/nano10101959. Q1, IF_{2024}: 4.3; number of independent citations: 13.
3. Bence Kutus, Csilla Dudás, **Eszter Orbán**, Alexandru Lupan, Amr AA Attia, István Pálinkó, Pál Sipos, Gábor Peintler, *Magnesium(II) d-Gluconate Complexes Relevant to Radioactive Waste Disposals: Metal-Ion-Induced Ligand Deprotonation or Ligand-Promoted Metal-Ion Hydrolysis?* Inorganic Chemistry, 58 (2019) 6832. https://doi.org/10.1021/acs.inorgchem.9b00289. D1 (Inorganic Chemistry)/Q1 (Chemistry), IF_{2024}: 4.7; number of independent citations: 7.

4. Lucian Baia, **Eszter Orbán**, et al., *Preparation of TiO2/WO3 composite photocatalysts by the adjustment of the semiconductors' surface charge*. Materials Science In Semiconductor Processing, 42 (2016) 66. https://doi.org/10.1016/j.mssp.2015.08.042. Q2, IF_{2024}: 4.6; number of independent citations: 38.

Not related research ΣIF=20.8

Total ΣΣIF=56.8

Conference proceedings:

1. **Eszter Kása**, Yvette Szabó, Judit Papp, Márton Szabados, Bence Kutus, Pál Sipos, *Synthesis, characterization and dissolution of bauxite residue (BxR) components relevant to acid neutralization - overview on a bottom-up study conducted at University of Szeged.* Conference Proceedings of the 12th International Alumina Quality Workshop, 2024.
2. Zsolt Kása, **Eszter Orbán**, Zsolt Pap, Imre Ábrahám, Mohit Yadav, Seema Garg, Klara Hernadi, *Effect of the different BiOI immobilization technique on the coverage of ceramic paper and the photocatalytic activity*. Progressive Trends in Coordination, Bioinorganic and Applied Inorganic Chemistry: Monograph Series of the International Conferences on Coordination and Bioinorganic Chemistry, 2019.
3. **Eszter Orbán**, Márton Szabados, Bence Kutus, István Pálinkó, Pál Sipos, *Comparison of kaolinites from different sources*. Progressive Trends in Coordination, Bioinorganic and Applied Inorganic Chemistry: Monograph Series of the International Conferences on Coordination and Bioinorganic Chemistry, 2019.

Conference participations related to the PhD dissertation:

E. Kása, I. Petri, M. Szabados, B. Kutus, P. Sipos, Modified sodalite with O-type additives for efficient removal of basic fuchsine dye from aqueous solutions, 18th European Student Colloid Conference, Szeged, 2022.
E. Kása, M. Szabados, B. Kutus, P. Sipos, Neutralization of tricalcium aluminate hydrates with hydrochloric acid, 20th International Symposium on Solubility Phenomena and Related Equilibrium Processes, Instituto Politécnico de Bragança, Portugália, 2022.
E. Kása, B. Kutus, P. Sipos, The synthesis and neutralization of hydroxysodalite, 28th International Symposium on Analytical and Environmental Problems, Szeged, 2022.
Kása E., Szabó Y., Szabados M., Kutus B., N. Bellahsen, Sipos P., A trikalcium-aluminát előállítása ipari körülmények között és semlegesítési folyamatainak feltérképezése, 55. Komplexkémiai Kollokvium, Debrecen, 2022.
E. Kása, M. Szabados, P. Sipos, Mechanochemical activation of kaolinite to manipulate the dissolution kinetics of the solid, 27th International Symposium on Analytical and Environmental Problems, Szeged, 2021.
E. Kása, Zs. Kása, M. Szabados, P. Sipos, Neutralization of tricalcium aluminate with various acids, Interdisciplinary Doctoral Conference, Pécs, 2021.

All conference participations:

Co-author of 15 lectures presented in international and Hungarian conferences.
Co-author of 7 posters presented in international conferences.

5. Magyar nyelvű összefoglaló

Az alumíniumiparban általában a Bayer-eljárás során a bauxitból alumínium-oxid keletkezik, majd a Hall-Héroult-elektrolízissel tiszta alumíniumot állítanak elő. Az előbbi folyamat melléktermékeként keletkezik, a mindenki által jól ismert vörösiszap, aminek magas pH-ja és nagy mennyisége számtalan katasztrófát okozott már világszerte. Bár az ipar és az akadémia komoly erőfeszítéseket tesz a vörösiszap mennyiségének csökkentése érdekében, még nem született meg egy globális, mindenki által elfogadható megoldás a problémára. Munkám során arra törekedtem, hogy megértsem a Bayer-eljárás során végbemenő folyamatokat, illetve feltérképezzem a melléktermékekben rejlő lehetőségeket.

Doktori munkám első részében különböző módon – kezeletlenül, mechanokémiai és/vagy termikus eljárással – előkészített kaolinitek oldódási kinetikáját vizsgáltam nátrium-aluminát-oldatban, amely összetételében az ipari Bayer-féle eljárásban használt oldatnak felel meg. Mivel a kaolinit a bauxit egyik fontos alkotóeleme, fizikai-kémiai jellemzői ipari szempontból meghatározóak. Különösen lényeges a kioldódott szilícium koncentrációja adott idő alatt, amely a kaolinit oldódásának, illetve az ebből keletkező szodalit képződésének sebességétől függ. A mechanokémiai kezelés például előnyösen módosíthatja a reakciókinetikát azáltal, hogy növeli a reaktív felületet és az aktív (savas) helyek számát, így elősegítve az alumínium- és szilíciumionok, valamint a hidroxidionok közötti kölcsönhatásokat és gyorsítva az oldódási folyamatot. Kísérleti eredményeim alapján a fizikai és kémiai átalakulások elsődleges hajtóerői a részecskék fragmentációja, delaminációja és az amorfizációval járó szerkezeti hibák megjelenése. Emellett az Al/Si−OH csoportok dehidroxileződése is érdemi mértékben járult hozzá ezekhez a változásokhoz.

A szodalit tulajdonságait jelentős mértékben befolyásolta a kiindulási kaolinit jellege, valamint az aluminát-oldatban jelen lévő szennyeződések összetétele. A szodalitot szerves szennyezők jelenlétében is előállítottam, és az így kapott termék adszorpciós képességét vizsgáltam a Basic Violet 14 (BV14) festék molekulára vonatkozóan. A kristályszerkezetre, az infravörös spektroszkópiai jellemzőkre, a morfológiára és az elemi összetételre vonatkozóan nem tapasztaltam számottevő eltérést a különböző minták között. Ezzel szemben a fajlagos felületük jelentős különbséget mutatott, amely erős korrelációt jelez a szerves szennyezők teljes mennyiségével – akár a szodalit felületéhez kötődve, akár a szerkezet pórusaiban elhelyezkedve. Ugyanakkor a vizsgálatok nem mutattak egyértelmű kapcsolatot a szodalit képződése közben jelen lévő szerves szennyezők és az adszorbeált festékmennyiség között. A szodalit adszorpciós kapacitását összehasonlítva egy azonos célra alkalmazott zeolitéval, megállapítottam, hogy a szodalit akár három-négyszer több BV14 megkötésére képes, annak ellenére, hogy fajlagos felülete jóval kisebb. Ebből arra következtethetünk, hogy az adszorpciós képesség nem a fajlagos felülettel, hanem nagyobb valószínűséggel a festékmolekulák és a pórusszerkezet méretbeli hasonlóságával van összefüggésben.

A disszertáció utolsó szakaszában a nagy tisztaságú trikalcium-aluminát-hidrát (TCA) előállítását vizsgáltam, olyan körülmények között, amelyek jellemzőek az alumíniumipari technológiákra. Az új szintetikus eljárással előállított TCA-t összehasonlítottam egy hagyományos módszerrel készített mintával, mely referenciaként szolgált munkám során. A fizikai és kémiai tulajdonságaikban nem találtam szignifikáns eltérést, és az oldhatóságuk is azonosnak bizonyult mind desztillált vízben, mind 1 M NaCl oldatban. Vizsgálataim kiterjedtek az 1 M HCl és a TCA közötti reakciómechanizmus tanulmányozására is, amely során egy új, irodalomban még nem publikált mechanizmust javasoltunk. Az eredmények szerint a TCA oldódását követően hidrokalumit (LDH) képződik, amelynek mennyisége a savkoncentráció növekedésével arányosan emelkedik. Semleges pH-nál (pH = 7) azonban már csak alumínium-hidroxid jelenik meg szilárd fázisként.

Alulírott **Dr. Sipos Pál**, mint *Kása Eszter* jelölt doktori témavezetője *A Bayer-féle timföldgyártás során képződő melléktermékek reaktív komponenseinek képződési és semlegesítési folyamatai, valamint adszorbensként történő felhasználásuk* című doktori értekezéshez kapcsolódó, lentebb felsorolt publikációkkal és a jelölt tézispontjaival kapcsolatban ezúton nyilatkozok arról, hogy az értekezésben felhasznált eredmények tükrözik a jelölt önálló hozzájárulását. A tézispontokhoz kapcsolódó eredmények elérésében a jelölt szerepe meghatározó fontosságú volt, ezért ezeket nem használtuk fel más tudományos fokozat megszerzésekor, és ezt a jövőben sem tesszük:

T1: Eszter Kása, Márton Szabados, Kornélia Baán, Zoltán Kónya, Ákos Kukovecz, Bence Kutus, István Pálinkó, Pál Sipos, *The dissolution kinetics of raw and mechanochemically treated kaolinites in industrial spent liquor – The effect of the physico-chemical properties of the solids*. Applied Clay Science, 203 (2021) 105994.

T2, T3: Eszter Kása, Kornélia Baán, Zsolt Kása, Zoltán Kónya, Ákos Kukovecz, István Pálinkó, Pál Sipos, Márton Szabados, *The effect of mechanical and thermal treatments on the dissolution kinetics of kaolinite in alkaline sodium aluminate solution under conditions typical to Bayer desilication.* Applied Clay Science, 229 (2022) 106671.

T4, T5: Eszter Kása, Ivett Petri, Márton Szabados, Áron Ágoston, András Sápi, Zoltán Kónya, Ákos Kukovecz, András Stirling, Pál Sipos, Bence Kutus, *Utilization of desilication products as efficient adsorbents for the removal of basic fuchsine.* Journal Of Hazardous Materials, 480 (2024) 136234.

T6: Eszter Kása, Yvette Szabó, Márton Szabados, Zsolt Kása, Zoltán Kónya, Ákos Kukovecz, Pál Sipos, Bence Kutus, *The neutralization of tricalcium aluminate hexahydrate and its spontaneous transformation into Friedel's salt, a layered double hydroxide*. Cement And Concrete Research, 177 (2024) 107414.