THE PROCURANCE AND THE USE OF CLAYS CHEMICALLY MODIFIED IN DECONTAMINATION PROCESSES

PLATON N. [1], SIMINICEANU I. [2], NISTOR D.I. [1], MIRON N.D.[1]

[1]University of Bacău, 157, Calea Mărăşeşti, 600115,Bacău,
nicoleta7platon@yahoo.com
[2]Université Technique Gh. Asachi, 71, Bd. Mangeron, RO-6600, Iaşi, Roumanie

Abstract
Pillared clays have drawn a great deal of attention, due to their catalytic and textural properties in different reactions. In this work we present a theoretical study regarding the process of clay pillaring in time inside the laboratory. One should consider extending it to the industrial level. The importance that pillared clays have on the protection of the environment is very high.

Key words: pillared, depollution, catalyst, processes, clay.

1. INTRODUCTION

Clay are mineral materials that is a part of the aluminum and silicate compounds, being subordinated to the mineralogical group of hydrate micas. Through the chemical modification of the interior structure, this gains superior properties. Hence, nowadays, national and international research aims at the obtaing of some chemically modified nanopurous clays that can be also used in the field of environmental depollution[1].

Pillared clays (PILC) became industrially important in 1970 due to their nanopurous structure and to their catalytic potential. The concept of transformation of solid materials that have layered structures into materials that have a porous one was first introduced by Barrer and MacLeon through the insertion of molecular species between the interlayered spaces of smectitic clay [2]. The name "pillared" has its origin in the work of Brindle& Semples and Vaughan& Lussier in 1970 on clay minerals, and the mechanism proposed for the ion exchange, followed by the retrieval of the solving agent [3].

2. METHODS OF PROCURANCE OF PILLARED CLAYS

Pillared mineral clays, are obtained through anorganic polymeric cations intercalation that change the compensatory cation by clay dehdroxylation and dehydration during calcinations, forming metal oxides groups that act as ,, pillars". These pillars separate the adjacent layers of silicates that enlarge the distance between the layers and create a permanent porosity between them.

The most important and the most used agent in the process of aluminum chloride pillared clay performing is Keggin polycation $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{+7}$ obtained from the basic solution of some aluminum chloride. The most indicated pillars proved to be the aggregate of metal oxides obtained from aluminum, zirconium, chrome, iron and titan polyoxides [4].

The clays pillaring, process has been studied over the years and developed at laboratory level and there is a tendency of it being extended to the industrial field. The laboratory method for the pillared clays obtaining is essentially based on the diluted clay suspension mixing pillared clay [5].

This ingenious and time-consuming process includes the following steps: the dispersal of clay into water, the preparation of a diluted pillared clay solution, the slow suppletion of the clay suspension, the washing through repeated centrifuging of the dispersion, the final washing through dialysis followed by a centrifugation, the drying of the obtained paste, the calcination of the dried product in order to obtain the pillared clay [6].

Obtaining pillared clay industrially meant the simplification of the laboratory steps. Thus one had to reduce the level of all the used reacting compounds. Vaughan (1988) was the first researcher to announce the successful preparation of a pillared 40% clay mud but without giving any details [4].

Molina and his partners (1992) published a book in which one show that concentrated clay mud (40% clay) was put in a dialyser and afterwards equilibrated in a pillared clay aluminum solution. The dialysis step is necessary in order to induce the insertion of pillars in the clay layered spaces, thus allowing the initial compensatory cation exchange to take place. They considered that, most likely, the dialysis permits the preparation of a very concentrated suspension and that it is necessary as it helps the classic exchange between Na^+ and Keggin ions $Al_{13}{}^{7+}$[4].

Schoonheydt and Leeman(1992) succeeded in preparing hydroxyl Al saponite by the adding of 6.5% clay powder in the solution used for the preparing of pillared clay [2]. This was the first case in which clay was added directly in the powder form. According to the results of the research (Schoonheydt et al., 1993), the pillaring process only takes place after the dialysis washing process. This process was not fully mastered and that is the reason of further more investigation necessity..[4].

Del Riego (1994) used this method in order to obtain natural pillared bentonite and purified natural 10% pillared bentonite. The study showed that the use of dialysis membranes helps the retrieval of the concentrated pillared material. At the same time, the number of washing times is reduced. Nevertheless it is a time consuming method and needs great quantities of solutions as the pillaring solution is diluted [5].

Schoonheydt (1994), also used dialysis in order to obtain saponite and pillared hectorit but using a diluted suspension 1 %(%mass) of pillared clay and a much diluted pillaring solution. The pillaring solution was prepared using the method of Furrer (1992) which shows the exclusive presence of Keggin ions. Afterwards one used different clay suspension concentrations and variable up to 0.8 M pillaring solutions in order to obtain purified saponite, hectorite and laponite but without using dialysis [6].

Thus, in the respect of reducing the pillaring process time, Fetter et al., (1997) introduced a new microwave irradiation method insertion step. One prepared Al pillared clay using a concentrated chlorhidrol solution (50%, 2.5M) and a clay suspension (50%) [7]. Moreno et al., (1997) tried to extend the methods of procurement of Al pillared montmorillonite obtaining and of pillared saponite through the adding of dried clay powder in the pillaring solution (diluted chlorhydrol), by obtaining filtering and by washing of the suspension in a press-filter [8].

Another study regarding this matter was mentioned by Frini and his partners (1997) , study that was dealing with the mixed Al/Cu pillared clay obtaining using three natural bentonites and comparing three methods: the use of clay powder, the concentration in a dialyser of clay mud and the classic dilution. Frini N. made this experiment considering the properties of mixed Al/Cu pillared clay. The pillaring process, there were used mixed agents likeAl-Me, in which case Me can be: Si^{4+},Cr^{3+}, Fe^{3+}, Fe^{2+},Ni^{2+}, Cu^{2+}, Zr^{2+}, La or Ce [9].

Lately, one has been using aluminum based pillaring products that can be found on the market. One also researched using 50% chlorhidrol in order to obtain Al pillared clay, Al-Fe suspension pillared clay obtained from suspensions of Ca-bentonite resulted from the adding of water (50%) or acetone (Storaro et al., 1998). The suspension, in acetone, was less viscous and easier to handle than the conventional watery suspension, according to the research of Storaro (1998) [10].

In 2003, Aouad.A, and his partners describe the optimum conditions for the preparation of Al pillared clay (PILC) in order to maximize the efficiency as far as time and water consumption are concerned, offering a possible extension to the industrial level at the same time. In order to (simplify) prepare PILC, they used natural clay, without chemically pre-treating or purifying it. The mixture of clay powder and solid Al_{13} was submitted to dialysis using a minimum volume of water. In figure 1, one presents a structural scheme of montmorillonite pillaring. This technique leads to the creation of a larger reactive surface which implies special features for this type of material. [11,12].

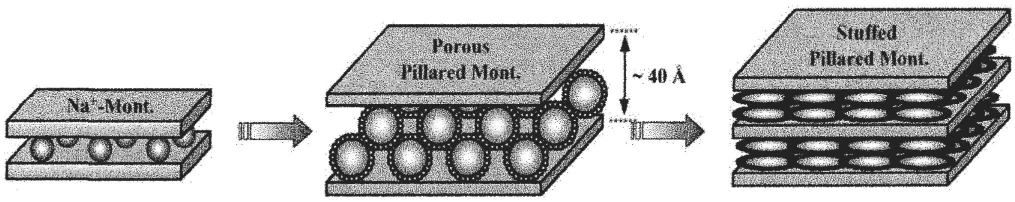

Fig.1. Structural scheme of montmorillonite pillaring [12]

3. THE USE OF CLAY IN ENVIRONMENTAL PROTECTION

The most important features of clay that make them to be used in varied fields are: high cationic exchange capacity, great expansion capacity, porosity, shape selectivity, osmotic shock and thermal stability and surface properties- absorption, specific surface, surface acidity. The properties of the resulted materials are mainly dependent on the type of the used clay, on the cations from the structure of clay and on the pillaring agents used during the process (they can be either organic or inorganic) [1,10,12].

Chemically modified clays has a depolluant feature not only due to their filtrate properties but also due to the fact that they are mainly aluminosilicates matrix that realize ionic exchange processes with the environment, retaining the harmful cations\ anions like heavy metals and radioactive elements. Due to the porosity of this substance one can use it as a molecular sieve, which is very important [7].

Clay based materials can also be used as a coagulant agents on account of their electro-chemical potential that they can develop on the exterior side, forming a double electric layer, especially if they are chemically and physically treated before going on with the experiment, thus helping the clotting which in its turn helps the efficiency of the filtering process [1, 8].

By chemically modifying of clays, the area of their application grows, including, amongst other things, the preparation of materials that have an increased value, and that are used in order to prevent pollution by the ion exchange. One also obtains catalytic materials, auxiliary materials for the alimentary and pharmaceuticals industries, and not long ago one also obtained micro porous materials that have multiple non-conventional uses.

Some authors say that one should also use cationic clays not only in preventing the pollution of the environment, but also in organic synthesis catalytic reactions, in cracking reactions and methane reforming reactions [1,4,11].

3. Conclusions

If we consider advantages and the disadvantages of the pillaring methods shown, one should be interested in the clays industrially preparing. The resulted materials have very well organized interlayer pillars and have a very rigid structure. In the future one should value more the indigenous clay materials that could be used in economic processes and that can prevent pollution. An exact analysis of the existing data in the domain of clays and of micro porous materials shows the importance of going on with this research.

Bibliography

[1]. Vaughan, D.E.W. *Pillared clays a historical perspective.* Catalysis Today 2, 1988, 187-198.

[2]. Molina, C.B., Vieira-Coelho, A., Poncelat, G. *Hydroxy-Al pillaring of concentrated clay suspensions*. Clays and Clay Minerals 40, 1992, 480-482.

[3]. Schoonheydt, R.A., Leeman, H. *Pillaring of saponite in concentrated medium.* Clay Minerals 27, 1992, 249-252.

[4]. Schoonheydt, R.A., Van Den Eynde, J., Tubbax, H. *The Al pillaring of clays.* Clays and clay Minerals 41, 1993, 598-607.

[5]. Del Riego, A., Herrero, I., Benito, I. *Preparation of PILC-Al through dialysis bags: a comparative study.* Applied Clay Science 9, 1994, 189-197.

[6]. Schoonheydt, R.A., Leeman, H., Scorpion, A. *The Al pillaring of clays*. Clays and Clay Minerals 42, 1994, 518-525.

[7]. Fetter, G., Heredia, G., Maubert, A.M. *Synthesis of aluminium-pillared montmorillonites using higly concentrated clay suspensions.* Applied Catalysis 162, 1997, 41-45.

[8]. Moreno, S., Gutierrez, E., Alvarez, A. *Al-pillared clays: from lab syntheses to pilot scale production; characterisation and catalytic proprties* Applied Catalysis 165, 1997, 103-114.

[9]. Frini, N., Crespin, M., Trabelsi, M., Messad, D. *Preliminary results on the properties of pillared class by mixed Al-Cu solution*, Applied Cxlay Science 12, 1997, 281-292.

[10]. Storaro, L., Lenarda, M., Puchini, V. *Hydroxyl Al-pillaring of concentrated suspensiom of smectite clays*. Microporous and Mesoporous Materials 20, 1998, 317-331.

[11]. Aouad, A., Mandalia T., Bergaya, F. *A novel method of Al-pillared montmorillonite preparartion for potential industrial up-scaling.* Applied Clay Science 28, 2003, 175-182.

[12]. Yang –Su, H., Yamanaka, S., 2006. Preparation and characterization of microporous SiO_2- ZrO_2 piilared montmorillonite. Journal of Solid State Chemistry 179, 2006, 1146-1153.