Study of Sorption Properties of Aluminium Oxides and Hydroxides Powders Obtained by Electro-Impulse Methods

S P Zhuravkov¹, G L Lobanova¹, D V Martemiyanov¹ and L V Nadeina²

¹ Institute of High Technology Physics, Research Tomsk Polytechnic University, 2A, Lenin Ave, Bld. 11, 634028, Tomsk, Russia
² Institute of Natural Resources, Research Tomsk Polytechnic University, 2A, Lenin Ave, Bld. 5, 634028, Tomsk, Russia

E-mail: zhursp@yandex.ru

Abstract. Experimental results of physicochemical and sorption properties of material samples obtained by electro-spark dispersion in water and by conductor electric explosion in argon are shown in the paper. Due to comparison of investigated samples sorption activity under static conditions, it was able to determine the most effective samples in the process of extraction of Cu²⁺ ions from aqueous solutions.

1. Introduction

The development of new kinds of nanomaterials and their properties investigation are of the main interest in recent years [1-8]. Oxide and hydroxide forms of aluminium obtained by water and aluminium electro-explosive powder interaction are of primary concern among well-known nanosized materials [9]. The advantage of this technology is that there are no alkali metal or ammonium cations when aluminium hydroxide precipitates. And this, in turn, provides high purity of product derived from electro-explosive powders. However, different conditions of the process of conductor electric explosion and post passivation of obtained nanosized metal powders result in, even in the same laboratory, the original metal powders vary in particle size and shape, and they also differ in surface condition, they vary in a fraction of metal phase in powder composition etc. Hydroxides are formed in the metal oxidation zone as a result of nanosized metal powder of aluminium and water interaction. Due to the fact that hydroxides have slight water solubility they are capable of producing high oversaturated solutions when the metal is oxidized intensively. That is why obtained products contain not only crystalline mass but cryptocrystalline and colloid ones. In spite of way of hydroxides formation in time especially under the air-dry condition, they lose capillary and adsorbed water forming chemically-combined hydroxide group compounds. Therefore, anhydrous oxides are formed which have property stabilized surfaces. Thus, comparative testing of their use as an active component of filter and sorption materials in order to clean water from microbiological pollution [10] and to treat sewage from heavy metals [11] is of the main interest.

Electric discharge metal dispersion is another method to obtain metal nanopowders using electric discharges. This method has been presented in sufficient detail in the papers [12-13]. Electric discharge metal dispersion is carried out in metal electrode when between metal electrodes there is a
metal load (in the form of granules or arbitrary shape particles size 5-10 mm) submerged in liquid (for example, in water). Therefore, dispersion of metal and producing fine metal particles and water interaction are not separated from each other as in the use of electro-explosive powders. In such kind of system electric breakdowns of some sections (as power fluid layers and thin oxide films on the surface of granules) between metal granules are due to impulses of voltage energizing electrodes. The breakdowns can be shown by way of multiple sparking (discharge channels). When applying practically voltage impulse parameters from 0.5 to 25 kV, range of sizes of finely dispersed metal particles is sufficiently wide within the interval from nanometer units to tens of micrometers. Being to the left of hydrogen in the line of metal activities the finely dispersed metal particles, forming and accumulating in investigated system, are oxidized and displace hydrogen from water [14]. Hydraulic shocks, accompanying electric discharges, maintain the finely dispersed metal particles in suspension. They help the diffusion processes to be easy at “surface of metal particle – water” boundary. They also provide accelerated development of oxidation-reduction reactions in the bulk suspension. At the same time the large-sized granules of metal loading remain at the bottom of reaction chamber. In electroerosion chamber the metal oxidation undergoes partially in the periods of electrodes voltage supply, partially it undergoes in the periods between impulses, and it continues after disconnection of voltage source when there is no electrode voltage. In this period the metal particle oxidation is carried out by chemical method at uncontrolled potential [14]. Therefore, according to the process for making products of metal load erosion – polydisperse metal particles – they, on the one hand, are acted upon by factors originated with a discharge channel both in solid and in gas and in liquid. But, on the other hand, the particles interact with water or solution at uncontrolled potential [12].

Hence, metal nanopowder method can effect on composition and properties of products which have been formed.

The aim of work is to compare and to estimate structural characteristic and sorption properties of both aluminium hydroxides, obtained by oxidation of aluminium electro-explosive and electroerosion powders and water interaction products, and active aluminium oxide for chromatography by containing Cu$^{2+}$ cation aqueous solution contact.

2. Experimental

Active aluminium oxide (sample 1 Table 1) was used as a comparison standard [15]. Sample 2 (Table 1) was obtained by aluminium electroerosion powder oxidation in water. Experimental apparatus reported in [12] was used to carry out electroerosion dispersion of aluminium load (granulated aluminium chemically pure grade) in water. After the treatment of aluminium load by electric discharges had been finished, suspension of eroded materials was separated from load by decantation and it was holding in touch with water until hydrogen stopped giving off at room temperature. Then the product was dehydrated and dried at 105°C.

Electro-explosive aluminium nanopowder, the initial particles of which had a size from 20 nm to 100 nm, was used to obtain aluminium oxyhydroxide (sample 3 Table 1). The initial particles are combined into aggregates with the size to 500nm and they are combined into loosely coupled aggregate agglomerates with the size to 5 µm. Average surface diameter of aluminium nanopowder particles is 110 nm. Aluminium nanopowder was previously passivated in air, and hereby the metal aluminium content 20nm was min 91% mass. Then aluminium nanopowder interacted with water according to the method of AlOOH nanofiber process used in the paper [9].

The thermal nitrogen desorption method was used to estimate structural characteristics of investigated materials. Samples of pores were tested with a help of analyser «SORBTOMETR-M», and specific surface (S) and specific volume of pores (P) were estimated according to measurement data.

Cu$^{2+}$ ion sorption was carried out under static conditions. Samples of 0.2 g materials were added to 20 sm$^3$ solutions (V) with different initial concentration ($C_0$) of adsorbed substances from 2 to 40 mg/dm$^3$. After carrying out this process during 150 minutes the solution was separated from sorbent with a
help of centrifugation rotating at speed of 20000 r/min, and adsorbed substances equilibrium concentrations \( C_p \) were determined. \( \text{Cu}^{2+} \) ion concentration was determined by method of stripping voltammetry with a help of a device with analyser TA-07. \( \text{Cu}^{2+} \) ion sorption was carried out in activated aluminium oxide – chromatographic standard sorbent – under similar conditions to quantify sorption properties of derived products [15].

Sorption capacity \( (\text{mg/m}^2) \) was calculated according to formula:

\[
A_p = \frac{(C_0 - C_p) \cdot V}{m \cdot S}
\]

Where: \( C_0 \) – initial concentration, mg/dm\(^3\); \( C_p \) – equilibrium concentration, mg/dm\(^3\); \( V \)– volume of solution, dm\(^3\); \( m \) – mass of sorbent, g; \( S \) – specific surface of investigated products, m\(^2\)/g.

3. Discussion of Results

Data of phase composition, specific surface, specific volume and average surface diameter of investigated sample pores are presented in Table 1.

| Number of sample | Sample | \( S_{yp} \), m\(^2\)/g | \( P \), cm\(^3\)/g | Average diameter of pores, nm |
|-----------------|--------|--------------------------|----------------------|-------------------------------|
| 1               | Standard (Al\(_2\)O\(_3\)) | 100\% | 194,33 | 0,083 | 1,722 |
| 2               | Al(OH) +Al(OH)\(_3\) +Al\(_2\)O\(_4\) | 24,1\% 66,1\% 9,7\% | 85,07 | 0,037 | 1,720 |
| 3               | Al(OH) +10,5\% Al(OH)\(_3\) | 89,5\% | 220,57 | 0,095 | 1,717 |

As shown in Table 1, the sample №3 possesses maximum specific surface and specific volume of pores. It is aluminium oxyhydroxide synthesized by water and aluminium powder interaction. This powder was obtained under argon with a help of conductor electric explosion technology consisting of two phases. Larger portion of product includes Al(OH), whose formation energy is less than Al(OH)\(_3\). Sample №2 contains similar substances in its composition but different ratio. This sample makes up 66\% of Al(OH)\(_3\) phase content. According to XRD data, nonstoichiometric oxide Al\(_{2,66}\)O\(_4\) was found out together with hydroxides in sample №2. Similar structure oxide was previously described in the paper [16]. Discharges resulting in erosion of metal are most likely to take part in hydrate formation process. Probably, this oxide formation is possible in vapour-gas bubble, when the discharge channel degenerates into the vapour-gas bubble. Oxide phase formation was observed due to electrical erosion of zinc load in water [17]. In comparison with sample №3, enumerated special characteristics of aluminium hydroxides obtained by electrical erosion in water have determined not only the change of phase composition of product but the change of structural characteristics – specific surface and volume of pores have decreased. Therefore, the conditions of nanodispersed powder obtaining influence on its interaction with environment, in particular, with water. So, the authors of paper [18] noted significant influence of aluminium oxyhydroxide synthesis conditions (the temperature of process, pH medium, time and temperature of precipitation ageing, temperature and time of samples treatment) on composition and properties of precipitations being formed when oxidizing conductor electric explosion aluminium nanopowder. Thus, investigated samples, obtained from aluminium with a help of electric discharges of different stages technology process, differ from
each other both composition and structural characteristics, and this, without doubt, must have an effect on properties of their surfaces.

Adsorption isotherms of Cu$^{2+}$ ions of investigated products and active aluminium oxide taken by us as a standard according to adsorption amount are presented in Figure.

Figure indicates that ions of Cu are the most actively sorbed on the surface of sample №2, which is a mixture of aluminium oxide and hydroxides. Sorption properties of sample №3 are close to standard.

4. Conclusions
1. It is found that according to structure and phase composition, the products of aluminium powders oxidized by water obtained by various electro-impulse methods are different.
2. Comparison tests of material samples obtained under static conditions in the process of extraction of Cu$^{2+}$ ions from aqueous solutions were carried out. It was shown, that the sample consisting of mixture of aluminium oxide and hydroxides, which was obtained under conditions of electrospark aluminium-in-water dispersion, is the most effective.

References:
[1] Lobanova G L, Zhuravkov S P and Pustovalov A V 2011 Izv. Vys. Ucheb. zav. Fizika. B.54 N.11/3 pp 168-171
[2] Romanov A N, Romanova N A, Yavorovskiy N A, Zhuravkov S P and Pustovalov A V 2012 Izv. Vys. Ucheb. zav. Fizika. B. 55 N 6/2 pp 225-230
[3] Yavorovskiy N A, Pustovalov A V, Lobanova G L and Zhuravkov S P 2012 Izv. Vys. Ucheb. zav. Fizika. B. 55 N 6/2 pp 236-243
[4] Fedushchak T, Vosmerikov A, Uimin M and Zhuravkov S Proceedings – 2012 7th International Forum on Strategic Technology, IFOST 2012 2012. C. 6357498.
[5] Fedushchak T A, Petenko T V, Vosmerikov A V, Kanashевич D A, Velichkina L M and Zhuravkov S P 2012 Russian J. of Physical Chemistry A. B. 86. N3 pp 375-379.
[6] Zhuravkov S, Plotnikov E, Martemyanov D, Yavorovsky N, Hasse U and Zander S 2014 Adv. Mater. Res. V 872 pp 74-78
[7] Lysenko E N, Surzhikov A P, Zhuravkov S P, Vlasov V A, Pustovalov A V and Yavorovsky N A 2014 J. of Ther. Anal. and Cal. V 115 Issue 2 pp 5-11
[8] Zaikovskii V I, Anufrienko V F, Kodenev E G, Echevskii G V, Vasenin N T, Ismagilov Z R, Parmon V N, Vosmerikov A V, Korobitsyna L L and Zhuravkov S P 2005 Dokl. Phys. Chem. V 404 N4-6 pp 201-204
[9] Pustovalov A V, Shiyan L N and Zhuravkov S P 2010 Sbornik trudov 3-y Vserossiyskoy nauchnoy konferentsii s mezhdunarodnym uchastiem. Nanomaterialy i tekhnologii. Nanostrukturirovannye sistemy v fizike kondensirovannogo sostoyaniya. Tekhnika i tekhnologiya nanomaterialov - Ulan-Ude, 26-28 avgusta 2010.- Ulan-Ude: Izd-vo Buryatskogo gosuniversiteta pp 126-131
[10] Martemyanov D V, Korotkova E I and Galanov A I 2012 Vestnik Karagandinskogo universiteta : Seriya: Khimiya V 67 N 3 pp 61-65
[11] Martemyanov D V, Galanov A I and Yurmazova T A 2013 Fundamental'nye issledovaniya N 8/3 pp 666-670
[12] Sergey Zhuravkov, Alexey Pustovalov, Galina Lobanova, Olga Kvashnina and Nikolay Yavorovsky 2014 Proceedings International Conference on Mechanical Engineering, Automation and Control Systems (MEACS) 978-1-4799-6221-1/14/$31.00 ©2014 IEEE.
[13] Evgenii Plotnikov, Sergey Zhuravkov, Andrew Gapeyev, Vladimir Plotnikov and Dmitry Martemyanov 2014 Adv. Mater. Res. V 1040 pp 65-69 Online available since 2014/Sep/24 at www.scientific.net
[14] Sharlo G. Metody analiticheskoy khimii. Izd-vo «Khimiya», M. - L., 1965 pp 152 - 205
[15] Oksid alyuminiya aktivnyy AOA-1 (GOST 8136-85)
[16] Shirasuka K, Yanagida H and Yamaguchi G. 1976 J. of the Ceramic Assoc. of Japan V 84 pp 610-613
[17] Galanov A I, Lobanova G L, Zhuravkov S P, Saprykin F E, Kornev Ya. I and Yavorovsky N A 2013 Russian J. Perspektivnye materialy N 4 pp 64-71
[18] Volkova G I, Sedoy V S 2008 Russian J. Zhurnal prikladnoy khimii V81 Vyp5 pp 721-725