Possibilities of Using Fly Ash with Other Industrial Waste to Obtain Geosorbents and Composite Materials

S L Fuks¹, S V Devyaterikova², S V Khitrin³
¹, ², ³ Vyatka State University, Moskovskaya street, 36, City of Kirov, 612100, Russia

E-mail: usr01730@vyatsu.ru

Abstract. The authors have studied the conditions of using waste obtained after thermal and chemical processing of minerals (coal, apatite, etc.) and unused natural polymer lignin formed as a result of wood hydrolysis. It has been established that these wastes, individually and in various combinations, can be used as an effective geosorbent for lanthanum ions from wastewater, in the form of composite electrochemical coatings and in the manufacture of ceramic products. The degree of trapping of lanthanum ions from concentrated wastewater with a mixture of fly ash and hydrolytic lignin reaches 96%. Internal stresses and microhardness of composite electrochemical coatings (CEC) nickel – fly ash decrease with increasing thickness and content of fly ash in the nickel layer due to the presence of 4.23% iron fraction with increasing its strength. The use of fluorogips and fly ash in the manufacture of mixtures for the production of ceramic products, including red brick, gives positive results in reducing shrinkage during high-temperature processing of the composite.

Introduction
Waste obtained during the processing of minerals is a source of secondary material resources, representing valuable raw materials, expanding the raw material base of industry. These wastes occupy large areas near enterprises and have a negative impact on the environment. In this regard, it is necessary to create and implement technological processes that dramatically reduce the amount of industrial waste due to their maximum utilization.

Among industrial wastes, the leading role in terms of formation belongs to fly ash and slags obtained from burning solid fossil fuels (coal) in thermal power plants (TPPs) [1-2], as well as gypsum and chalk from mineral processing (apatite, fluorite, phosphorite, limestone) at chemical plants engaged in the production of fertilizers and fluoropolymers. The formation of ash and slag exceeds 10 million tons, of hydrolytic lignin - 1 million tons, gypsum and chalk reaches hundreds of thousands of tons per year only at the enterprises of Kirov and Kirovo-Chepetsk.

Huge quantities of this waste have been accumulated in dumps and sludge accumulators occupying valuable land. The maintenance of sludge collector gypsum and ash and slag landfills requires significant costs and is a source of environmental pollution. At the same time, these products are materials that have undergone chemical and high-temperature processing, have specific properties, and can be effectively used for the production of various composite materials, including cement, clinker-free binder, ceramics, catalysts, geosorbents, coatings and other target products [3-12].
Taking into account the large reserves of these wastes and the need for demanded ecologically safe products, the purpose of this article is to study the possibility of using these problematic industrial wastes for the manufacture of composite materials: an effective adsorbent for purifying wastewater from various industries, solutions and gases, red brick, ceramics, chemical and electrochemical composite coatings.

**Experimental Techniques**

The study of the morphology of ash particles and its chemical composition was performed by scanning electron microscopy (SEM). The image was obtained using the Sem main menu. X-ray microanalysis was used to determine the content of chemical elements. For this purpose, an energy dispersive X-ray microanalysis (ERM) sensor embedded in an SEM was used. Sewage treatment (E) from lanthanum ions (3+) was carried out by adsorption of pollution by fly ash formed during the coal combustion in the Kuznetsk basin.

The effect of the introduction of the dispersed phase of fly ash on the quality of the composite electrochemical coating (CEP) was evaluated by the current yield of nickel, which was calculated by the formula:

$$BT_{Ni} = \left( \frac{\Delta m_{pr}}{m_{theor}} \right) \times 100 \%,$$

where $\Delta m_{np} = (m_2 - m_1) - m_{ash}$, and the difference $(m_2 - m_1)$ is the mass of CEC, $m_{ash}$ is the mass of fly ash.

The value of the theoretical mass was calculated according to the second Faraday law:

$$M_{theor} = k \times I \times \tau,$$

where $k = 1.095$ g/A·h – is an electrochemical equivalent,

$I$ - current strength, A,

$\tau$ - time, h.

The microhardness of the coating was determined by the Vickers method using a PMT-3M microhardness meter.

**Experimental results and discussion**

**Use of secondary products as lanthanum sorbents**

The isolation of lanthanum (3+) from catalyst wastes and leaching of apatites and other materials made it possible to obtain pure salts, including the chloride-containing salt LaCl$_3$ which is soluble in concentrated solutions [9-10]. This salt, when used as a component of an electrolyte for deposition of composite coatings on a metal base, makes it possible to obtain high-quality mixtures of a deposited metal and a dispersed phase embedded in it. The production of composite electrochemical coatings (CEC) is connected with the formation of a large amount of wash water, which should be cleaned of contamination with heavy metal ions, including lanthanum (3+). For this purpose, the authors [13–14] used the sodium hydroxide-treated anion exchanger AB-17-8, as lanthanum hydroxide particles La(OH)$_3$ are formed on the surface of the granules. Lanthanum was isolated from acidic solutions using KU-2 cation exchanger [15]. However, the physicochemical process of capturing La$^{3+}$ can also be carried out in a different way — using heat engineering and biotechnological production wastes, such as fly ash from coal combustion and lignin from the process of sulfuric acid hydrolysis of wood. To study the adsorption properties of fly ash with a particle size of 90-1200 μm, we used columns with a sorbent content of 75 g. To increase the flow rate of waste water through a column, fly ash was mixed in a 1: 1 ratio with larger particles of hydrolytic lignin of the same mass. The efficiency of
cleaning waste water containing lanthanum ions (3+) in the amount of 44.4 mg / l is presented in Figure 1.

![Figure 1](image)

**Figure 1.** The dependence of the efficiency of wastewater treatment on the concentration of La$^{3+}$ by fly ash oca (●) and a mixture of fly ash and lignin (○).

From the figure it can be seen that the efficiency of wastewater purification from lanthanum ions (3+) is higher when using fly ash, while mixing sorbent with lignin reduces this indicator. It increases the possibility of trapping biologically active heavy metals.

The value of the maximum permissible concentration (MPCr.h.) of lanthanum (3+) is 0.1 mg/l. Calculations showed that MPCr.h. is achieved by passing 2 liters of waste water with La$^{3+}$ content of 44.4 mg/l through a column with pure ash. If a mixture with lignin is used, the mass of sorbent must be increased by 8 times, but the speed of water flow will increase. For desorption of lanthanum (3+) from the sorbent, hydrochloric acid was used. The degree of capture was 96 %.

**Using fly ash as a component of composite electrochemical coating on a nickel matrix**

CEC, consisting of a nickel matrix and a magnetic fraction of fly ash incorporated into it, was applied to nickel-plating electrolytes. The composition is presented in Table 1.

| Electrolyte | Component                          | Концентрация, г/л |
|-------------|-----------------------------------|-------------------|
| №1          | Nickel sulfate                    | 250-300           |
|             | Nickel chloride hexahydrate        | 50-60             |
|             | Boric acid                        | 25-30             |
| №2          | Nickel chloride hexahydrate        | 300               |
|             | Boric acid                        | 20                |
|             | Ammonium chloride                 | 20                |
|             | Lanthanum chloride hexahydrate     | 0-13              |

The process temperature is 45-55 °C, pH of the solution is 3,5-4,5. Fly ash content is 20 g/l.

Figure 2a shows quantitative characteristics of the CEC of nickel-fly ash obtained during the precipitation from sulfate electrolyte No. 1, Figure 2b – from chloride.
Figure 2. The dependence of the current efficiency of nickel (○) and nickel in the CEC nickel-ash fly ash (●) on the current density of electrolytes No. 1 (a) and No. 2 (b).

Figure 2a shows that the nickel current efficiency reaches 98%, and for CEC nickel-fly ash the maximum current efficiency is lower and amounts to 65-66% at a current density of 0.5 A/dm², then decreases to 45-52% and remains almost constant in the range of current densities 1-3 A/dm².

Figure 2b shows that the current efficiency of nickel is 80-94% in a wide range of current densities, regardless of the presence of fly ash.

The fly ash content in CEC depends on the composition of the electrolyte, the current density and the time of deposition. Figure 3 presents the results of calculations of the average layer thickness depending on the content of fly ash in the CEC obtained from electrolyte No. 1.

Figure 3. The dependence of the thickness of the ash layer on the content in the CEC.

The calculated thickness of the ash layer in the coating increases with increasing amount of fly ash in the CEC, reaching 13 microns. It is especially important when obtaining thick-layer CEC. The influence of the composition of electrolyte No. 2 on the content of fly ash in the CEC is presented in Table 2.

Table 2. The dependence of the fly ash content in the CEC from the amount of lanthanum (3+) in the nickel plating electrolyte (electrolysis time is 20 min, current density is 2,5 A/dm²).

| Content of lanthanum (3+), g/l | 0  | 2,10 | 3,47 | 4,86 |
|-------------------------------|----|------|------|------|
| Fly ash content in the CEP, % | 1,67 | 2,34 | 2,62 | 1,82 |
As it can be seen, the fly ash content in the CEC is maximum in the concentration range of lanthanum (3+) equal to 2.1–3.47 g/l. Higher or lower lanthanum content (3+) leads to a decrease in the content of the dispersed phase in the coating.

Figure 4 shows the dependences of the microhardness of the nickel coating and CEC nickel-fly ash on the thickness of the coating obtained from electrolyte No. 1, Table 3 – from electrolyte No. 2.

![Image of Figure 4](image)

**Figure 4.** The effect of nickel precipitation thickness (○) and CEC nickel-fly ash (●) on their microhardness in electrolyte No. 1

It has been established that the microhardness of a nickel coating obtained from electrolyte No. 1 increases with an increase in the coating thickness to 10 μm and then remains almost constant (0,22-0,25 H/μm²). The microhardness of the CEC nickel-fly ash also depends on the thickness of the coatings. However, in this case, the maximum microhardness is observed at minimum thicknesses (3–6 μm), then decreases and at a nickel thickness in the CEC of 10–28 μm, it is 0.15–0.11 N/μm². The complicated course of the dependence is due to different nickel contents and the presence of a fraction of magnetic iron in the coating (on average, 4.23%) [16], having a microhardness of 0.15 N/μm² [16], which is lower than the nickel microhardness (0.17 N/μm²) by 12 %.

**Table 3.** The influence of the content of the dispersed phase and lanthanum ions (3+) in electrolyte No. 2 on the microhardness of the coating (electrolysis time is 20 min, current density is 2.5 A/dm²).

| Fly ash content, g/l | 20 | 0 | 20 |
|----------------------|----|---|----|
| Concentration of lanthanum (3+), g/l | 0 | 3,475 | 3,475 |
| Microhardness of the coating, N/μm² | 0,535 | 0,410 | 0,262 |

The table shows that the microhardness of the CEC from an electrolyte without lanthanum is 2 times higher than in its presence.

Table 4 shows the average elemental coating compositions of nickel and CEC nickel-fly ash, obtained from electrolytes No. 1 and No. 2 at a current density of 2.5 A/dm² and a time of electrolysis of 20 minutes.

It is shown that the nickel content in the coating is 77.74-91.61%, in the CEC it is 27.58-31.7% less, which is compensated by the components of fly ash: carbon (7%), oxygen (8.61-16, 55%), aluminum (1.59-4.01%), silicon (2.9-5.24%), sulfur (0.13%) iron (0.58%), and other impurities (0.16%), while reducing chlorine and alkali metals by 2%. With increasing coating strength, the protective properties of the CEC do not deteriorate.
Table 4. The elemental composition of the nickel coating and CEC nickel-fly ash.

| Electrolyte          | The content of elements in weight % |
|----------------------|-------------------------------------|
|                      | Ni   | C       | O     | Na  | K | Al | Si | S | Cl | Ca | Mg | Fe | Impurities |
| №1                   | 77,74 | 15,94   | 3,75  | 1,95 | - | -  | -  | 0,52 | 0,12 | - | -  | -  |
| №1 + fly ash 20 g    | 46,05 | 22,83   | 20,3  | 0,44 | 4,01 | 5,24 | 0,13 | 0,03 | 0,28 | 0,58 | 0,16 | -  |
| №2                   | 83,19 | 3,60    | 4,62  | 0,39 | 0,05 | -   | -   | 7,75 | -   | -  | 0,09 | -  |
| №2 + fly ash 20 g    | 78,52 | 5,46    | 4,65  | 0,10 | 0,03 | 4,26 | -   | -   | 1,92 | 8,46 | 0,04 | -  |
| №2 + La3+ 3,475 g/l  | 91,61 | 4,82    | 5,49  | 0,11 | 0   | 0,10 | -   | -   | 0,08 | -   | 0,04 | -  |
| №2 + fly ash 20 g + La3+ 3,475 g/l | 64,03 | 12,75   | 14,10 | -   | 1,59 | 3,00 | -   | -   | 0,68 | 3,19 | 0,29 | -  |

Using fly ash and fluorogips in the production of building products

Using wastes from chemical and energy enterprises in the production of building products reduces the technogenic load on the territories occupied by slag-ash wastes and sludge [17-19]. Currently, we are working on the joint use of fly ash and fluorogips, obtained from the production of mineral fertilizers from apatite raw materials [20, 21]. The results of determining the element composition of sludge from various enterprises are given in table 5.

Table 5. The element composition of the sludge production of mineral fertilizers.

| Production                  | The content of elements in weight % |
|-----------------------------|-------------------------------------|
|                             | C       | O     | Si       | S       | Ca    | Fe | Al |
| LLC “ZMU Kirovo-Chepetsk”   | 10,98   | 50,17 | 0,06    | 18,09   | 20,7  | -  | -  |
| LLC “URALHIM”, Perm         | 7,65    | 52,13 | 0,21    | 19,06   | 20,76 | 0,06 | 0,13 |

The table shows that the gypsum waste contains mainly calcium sulphate and, to a lesser extent, carbonates. The waste of URALHIM is characterized by the presence of clay, which is indicated by the presence of iron, aluminum and high silicon content in the sludge.

When producing ceramic products, including facing red brick, their shrinkage (volume change) after heat treatment is sequentially from 400 to 900 °C is of great importance. The results of determining the shrinkage of the product during the heat treatment process are presented in Table 6.

Table 6. Dependence of brick shrinkage on the content of fly ash and fluorogips.

| № of sample | 1  | 2  | 3  | 4  | 5  |
|-------------|----|----|----|----|----|
| Content *, %| 14,6 | 17,1 | 15,2 | 23,2 | 15,6 |
| Ash - 10,4 | -  | -  | -  | -  | -  |
| Total shrinkage in volume, % | 8,29 | 5,32 | 5,13 | 4,78 | 0,79 |

Note: * clay, ground brick, sand, water are the rest.
It was found that the smallest shrinkage was observed in samples containing equal amounts of gypsum and fly ash (samples No. 4 and No. 5). Reducing the amount of fly ash in the mixture in 1.5-3.0 times (samples No. 1 to No. 3) leads to an increase in shrinkage (Table 6).

Thus, it is possible to obtain a number of materials using secondary products or in combination with the target products, or in a mixture with other secondary components. In addition, this approach increases the environmental security.

References
[1] Krylov D A, Sidorova G P 2014 Ways to reduce the environmental impact on the environment of thermal power plants. Mining information and analytical newsletter Scientific and technical journal 6 pp.277-285.
[2] Sidorova G P, Krylov D A, Yakimov A A 2019 Environmental impact of coal-fired thermal power plants on the environment Bulletin ZabGU 9(124) pp. 278-38.
[3] Fomenko E V, Kondratenko E V, Salanov A N , Bajukov O A , Talyshev A A , Maksimov N G. 1998 Catalysis Today 42(3) pp.267-272. DOI:10.1016/S0920-5861(98)00101-1.
[4] Anshits A G, Nizov V A, Kondratenko E V, Fomenko E V 1999 Chemistry for sustainable development 7(2) pp. 105-118.
[5] Emelyanov V S, Shakieva T V, Shakiev E M, Dosumova B T, Dzhatkambaeva U N, Aybuldinov E K 2014 Using fly ash from thermal power plants to produce a catalyst for the oxidation of methanol to formaldehyde Basic research. Chemical sciences 9 pp. 1230-1236.
[6] Entin Z B, Nefedova L S, Strzhalovskaya N V 2012 Ash of TPP are raw materials of cement and concrete Cement and its use 2 pp.40-46.
[7] 7. RF patent №2524733. Raw mix for the manufacture of wall ceramic products. Priority of 03/26/2013. Posted on 10.08.2014. Bul. № 22.
[8] Arsentiev V A 2016 New technology of dry enrichment of fly ash from coal power plants based on applied mineralogy methods / V.A. Arsentiev, E.L. Kotova Notes of the Mining Institute 220 pp.521-525. DOI 10/18454/PMI.2016.4.521.
[9] 9. Kozlovskaya I.Yu., Martsul V.N. // The selection of lanthanum from spent catalyst for the cracking of petroleum hydrocarbons. Chemistry and technology of inorganic materials and substances. Works of BSTU. 2012. №3. pp.62-65.
[10] Levchenko E A 2014 The use of fluorogips to obtain a mineral binder Herald of ISTU 6 pp. 123-125.
[11] The patent of the Russian Federation №2380177. A method of processing fluorogips. Priority from 09/22/2008. Posted on 1/27/2010. Bul. №3.
[12] Patent No. 2408549. A method for producing a gypsum binder. Priority 10/19/2009. Published 10.01.2011.Bul. №1.
[13] Buzko V Yu, Sukhno I V, Buzko M B, Polushin A A, Panyushkin V T 2008 Study of the structure and stability of aque ions La (H2O) n3 + (n = 8.9) using ab initio methods Journal of neorgan. Chemistry 53(8) pp. 1342-1349.
[14] Bovina E A, Konstantinova M M, Tarasova D V, Chibirova F Kh 2015 Synthesis and study of lanthanum hydrosols obtained by the ion-exchange method Fundamental and applied research in the modern world. Proceedings of the XII International Conference 1 pp.5-12.
[15] Papkova M V, Mikhailichenko A I, Konkova T V 2016 Sorption extraction of rare-earth metals and other elements from phosphoric acid solutions Sorption and chromatographic processes 16(2) pp.163-72.
[16] Grigorovich V K 1976 Hardness and microhardness of metals. M. Science 230 p.
[17] Fux S L, Devyaterikova S V, Musikhina T A 2018 Geosorbent based on the combination of Kuznetsk-basin coal fly ash with various kinds of ligni IOP Conference Series: Earth and Environmental Science (EES).
[18] Patent number 831735. The method of producing fluorogips. Priority 23.02.1976. Published 05/23/1981. Bul. № 19.

[19] Patent number 2440940. Method of utilization of fluoroanhydrite. Priority 01/20/2010. Posted on 01/27/2012. Bul. №3.

[20] Patent number 1439092. A method of processing apatite. Priority 12/18/1985. Published 223.11.1988. Bul. №43.

[21] Solovev D B, Shadrin A S 2017 Instrument current transducer for measurements in asymmetrical conditions in three-phase circuits with upper harmonics International Journal of Electrical Power and Energy Systems 84 pp. 195-201. [Online]. Available: http://dx.doi.org/10.1016/j.ijepes.2016.05.012