Waste from the chemical industry of the Luhansk region is a source of critical raw materials

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Introduction

The main goal of the Communication "Critical Raw Materials Resilience: Charting a Path towards greater Security and Sustainability" is to provide the European industry with the necessary raw materials. The list of critical materials includes such metals as magnesium, cobalt, vanadium, platinum group metals etc.

In Ukraine, the amount of accumulated industrial waste is one of the largest in the world, among them approximately 51% is waste containing metals and their compounds - salts, oxides, and hydroxides. A significant part of these wastes is dangerous for the environment.

Sources of secondary raw materials containing CRM can be industrial waste from the chemical and petrochemical industry. In practice the content of metals listed as critical in waste is often higher than in natural raw materials.

Results & Discussion

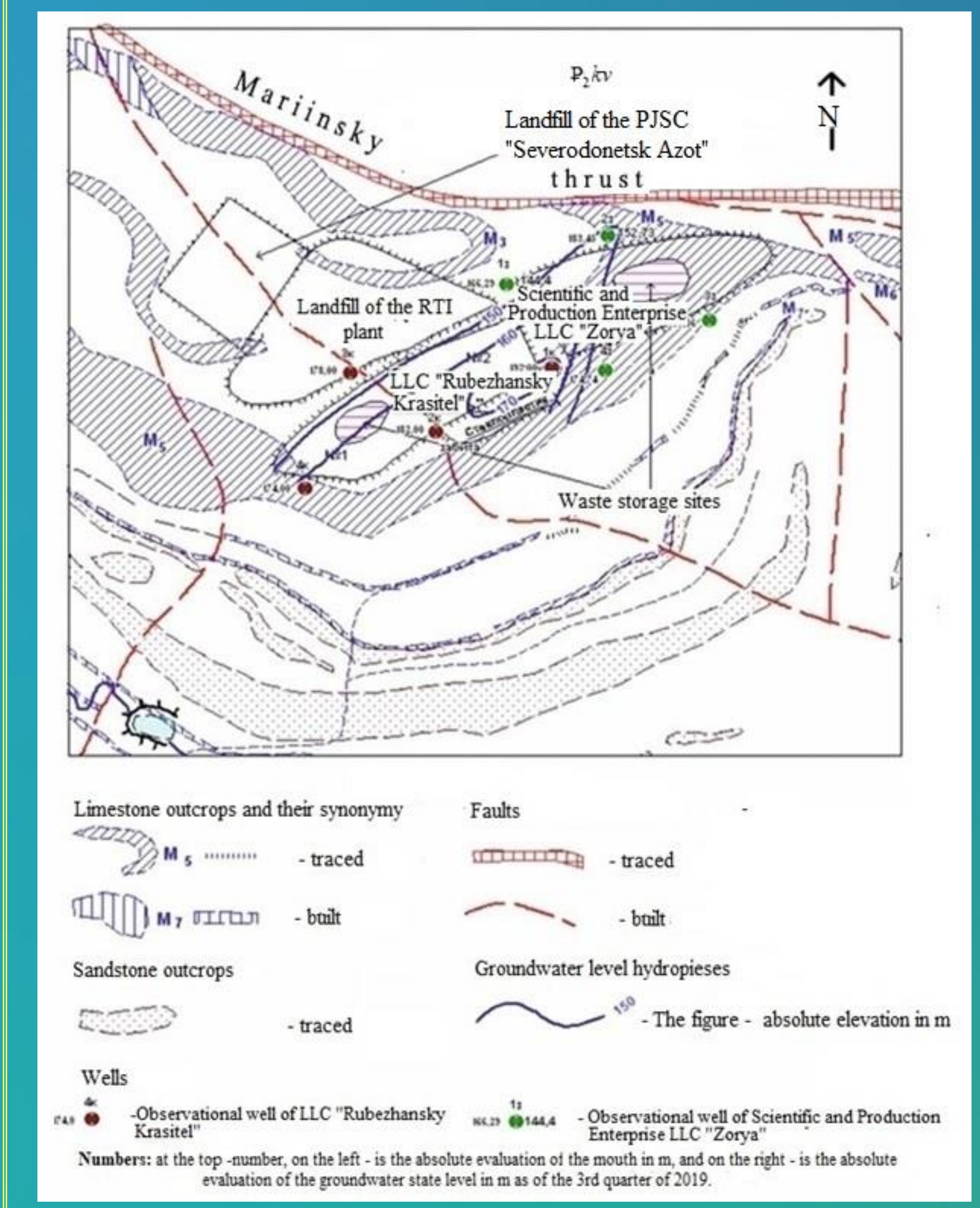

Fig.1 The map of industrial waste disposal site

In the Luhansk region, there are several large so-called "man-made deposits" - industrial waste landfills. One of the largest industrial waste landfill of PJSC "Severodonetsk Azot", is located near the village of Vovchoyarivka. Waste from chemical industry enterprises of the Rubizhansk-Lysychansk region has accumulated on the territory of the landfill. As of 2020, waste removal into the landfill was carried out by PJSC "Severodonetsk Azot" and Scientific and Production Enterprise LLC "Zorya", in previous years by Rubizhansky Krasitel, Lysychansk' Manufacture of rubber and technical products", LLC "NVO Severodonetsk Skloplastik" and others. The total amount of waste accumulated from the activities of theese is 375,268,749 tons. Some of them had ceased production.

Long-term operation (38-52 years) led to the loss of waterproofing properties of landfill structures, and, as a result, the inflow of hazardous substances into unprotected aquifers and contamination of local sources of water supply - wells in the village. Vovchoyarivka, which drains groundwater of beam alluvium and carbon weathering zones. The presence of pollutant components of various hazard classes in well water, which led to its unsuitability for drinking water supply, is a consequence of the impact of accumulators located within the boundaries of the landfill and located upstream of the groundwater flow.

Accumulation of industrial waste from various chemical enterprises on a single site of a landfill can lead to successive occurrences of accidents at these facilities and provoke an increase in their impact, causing the so-called "domino" effect.

Therefore, waste processing can solve not only the problems of raw material sustainability but also reduce the anthropogenic impact on the natural environment, and improve the condition of water bodies and the quality of drinking water.

An approximate list of components of spent catalysts and sludges (sources of CRM) is presented in Table.

Components of wastes

Waste types	Source	Components
Spent silver catalyst	Scientific and Production Enterprise LLC "Zorya"	Ag
Spent catalysts AVC-10, IK-1-6	Scientific and Production Enterprise LLC "Zorya"	V_2O_5
Spent catalysts from ammonia, methanol, acetic acid, nitric acid manufactures	PJSC "Severodonetsk Azot"	Co, Mo, Ni, V_2O_5
Water Treatment Plant wastes	PJSC "Severodonetsk Azot"	$CaCO_3$, $Mg(OH)_2$, NOM, and admixtures of Sr,

Vanadium-containing catalysts at the facilities of LLC "Zorya" and PJSC "Severodonetsk Azot" differ in chemical composition and content of CRM, at the first enterprise the catalysts were used for contact oxidation of sulfur (IV) oxide and contained 7-10% V_2O_5, at the other enterprise they were used for purification exhaust gases from nitrogen oxides and contain 12-15% V_2O_5.

Silver catalysts contain 7-20% silver depending on the process in which they were used at Zorya LLC.

The solution to the problem is in the processing of waste into marketable products. Two possible schemes for processing waste into marketable products are presented below. Wastes that can be processed according to such schemes should have a relatively stable chemical composition. Spent catalysts and sludges from water treatment and wastewater disposal meet these requirements.

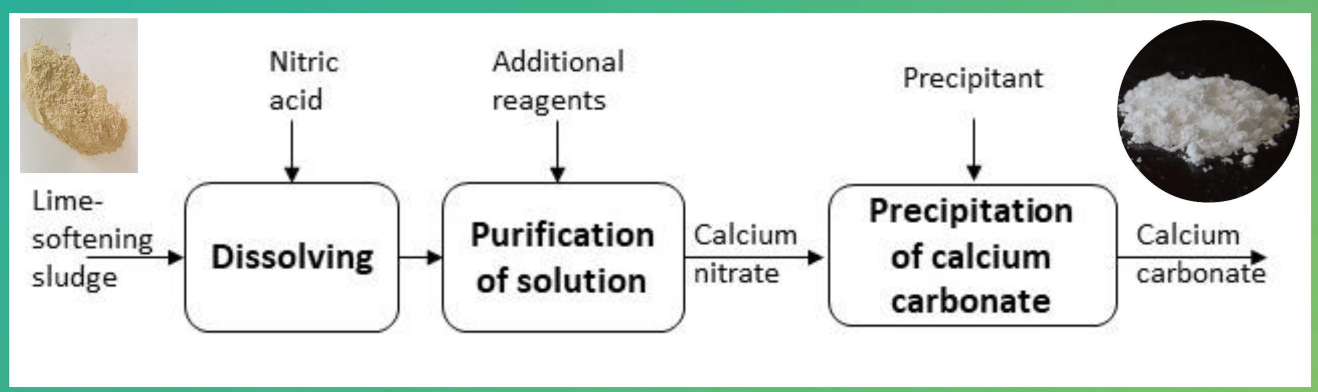

Fig. 2 The proposed scheme of water treatment waste processing

The water treatment waste of Severodonetsk Azot PJSC has a constant composition. The amount of magnesium in them (MgO) ranges from 6 to 17%, and calcium carbonate (~75%). They also contain coagulant residues in the form of ferric hydroxide and aluminum hydroxide and other components, including a small amount of strontium 1-5 grams per 1 kg of waste.

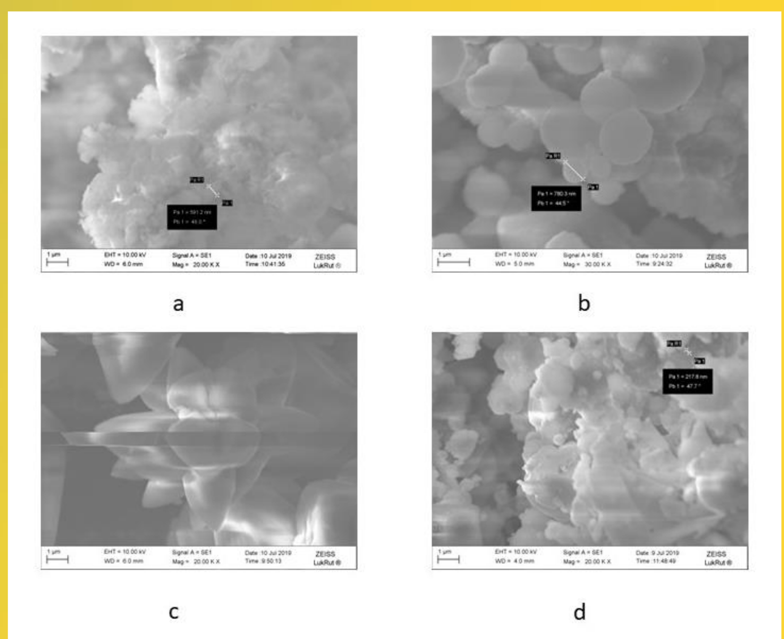

Fig. 3 SEM images of a) water treatment waste; b) $CaCO_3$ obtained by precipitation of Na_2CO_3; c) $CaCO_3$ obtained by precipitation with urea; e) $CaCO_3$ obtained by a mixed method.

The transformation of waste into purer calcium carbonate can be visually monitored using SEM images. Crystal morphology is quite different on all samples. Waste has different particle sizes, as it is formed as a result of coagulation in a natural way. Particles of calcium carbonate precipitates, obtained by precipitation of sodium carbonate, have a rounded shape. Precipitates formed by urea have plate-shaped particles that are combined into flower-like structures. According to the mixed method, which was carried out by successive precipitation with both reagents, crystals of various shapes were obtained.

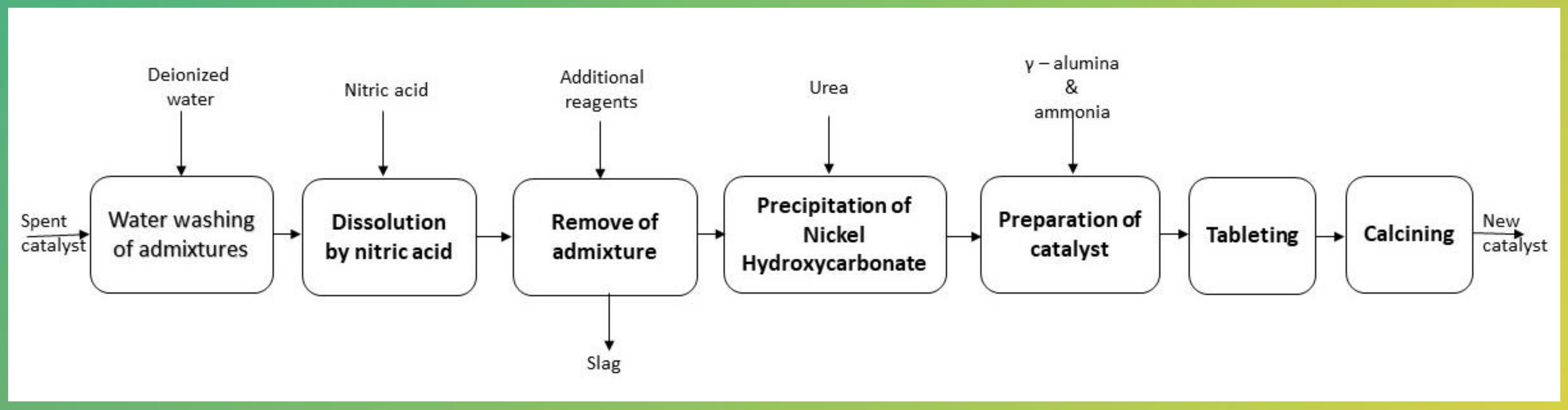

Fig. 4 Scheme of processing spent aluminum-nickel catalyst

As a result of the processing, the nickel compound was successfully separated from other components, and nickel hydroxycarbonate, a precursor for a new catalyst, was obtained. The specific surface of catalyst turned out to be 22-24% greater than the surface of the sample prepared from industrial reagents.

Conclusions

Absolutely, before use, the waste stored at the landfill should be inventoried in detail, including storage conditions. Before the war, this work was part of the smart specialization program of the region.

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