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

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The chemical composition and capacity of one of the largest storage facilities for industrial waste in the Luhansk region is described. Its impact on the environment is characterized. Using the example of spent catalysts and industrial water treatment waste, the possibilities of using certain types of waste to obtain marketable products are shown. Steps to solving environmental problems and extracting critical raw materials are proposed. Waste can be used for the production of catalysts and other materials in the processes of organic synthesis and biomass processing.

Keywords: critical row materials, waste storage, spent catalysts, catalyst for organic synthesis, marketable products, mathematical model

1. Introduction.

In September 2020, the European Commission adopted the Communication "Critical Raw Materials Resilience: Charting a Path towards greater Security and Sustainability", which defines a list of critical raw materials (CRM) that are recommended to be extracted from secondary raw materials. The main goal of the directive 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 addition to the materials listed as CRM, the European industry needs metals and minerals for the production of renewable energy. Therefore, it is predicted that by 2030, the annual demand for a wide range of special metals, as well as for iron, copper, zinc, and nickel, will increase significantly.

The main consumer of CRM in Europe is the industry. Thus, cobalt is most often used for the needs of metallurgy, for the production of special alloys, and also in the chemical industry as a catalyst or pigment (Deetman SEBASTIAAN et al., 2017). The demand for most metals from the CRM list is growing every year. Since the EU does not have or has an insufficient amount of CRM, there is a need to find new sources of their supply (Anna LADENBERGER et al., 2018).

Among the materials, there are those used for the chemical and pharmaceutical industry. Examples of the use of critical materials can be catalysts for carrying out cascade reactions, including in their composition Pd and Ru as CRM (Dhakshinamoorthy and Garcia, 2014). Also, there is a possibility of using Pt and Ru in green processes for pharmacy, for example, for processing cellulose into alcohol (Fukuoka and Dhepe, 2006). In addition to metals from the list of CRM, nickel and calcium carbonate are part of the API production catalysts (Busacca et al., 2011). The properties of catalysts are very important in the case of fine organic synthesis, for example, much attention is paid to the use of nanosized catalysts (Hariharalakshmanan et al., 2022). The use of catalysts containing metals from the CRM list is also relevant for modern technologies of processing biomass into marketable products (Luque, 2014).

It should be noted that in Ukraine, as in many countries, waste landfills are territorially close to industrially developed and mining regions, with a high level of man-made effect on the geological environment. Such regions often have complex geological conditions, which are determined by the significant development of tectonic disturbances and dangerous geological processes and are characterized by weak protection of the geological environment from technogenic influence.

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 ("Register of waste generation, treatment and disposal facilities of Luhansk region (as amended in 2017)," 2017).

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.

A rather large content of such metals as cobalt, vanadium, and nickel is characteristic of spent catalysts of the nitrogen industry and organic synthesis.

For comparison, natural sources of vanadium are phosphate rocks, including titanomagnetite and siltstone. Its content in these rocks is less than 2% (GOVERNMENT PUBLISHING OFFICE, 2018). Most often, cobalt is obtained as a by-product of the production of copper or nickel, its content in industrial ores is 1-2%. As for silver, it was the main product in only a few mines. It is mostly obtained as a by-product in the extraction of copper, gold, and from lead-zinc mines.

Nevertheless, there are obstacles in the use of waste, for which there are several reasons: insufficient motivation of producers for recycling, lack of effective recycling technologies, difficulty in sorting waste stored in landfills, etc. Technological utilization and careful separate storage of waste guarantee their further use.

Some of the accumulated waste may be later processed into useful products of commercial quality, but this will require a number of efforts. From the beginning, it may be necessary to make an inventory of landfills and determine ways of processing waste. Technological utilization and careful separate storage of waste will guarantee their further use.

2. Materials and methods

According to the waste register of the Luhansk region, a list of waste and the name or purpose of spent catalysts was determined (“Register of waste generation, treatment and disposal facilities of Luhansk region (as amended in 2017),” 2017). The approximate value of the content of the CRM is determined by names and purposes.

The waste, the chemical composition of which is mentioned in the work, was obtained from PJSC Severodonetsk Association "Azot", immediately before its storage at the landfill. Determination of the content of the main components of water treatment waste was carried out by complexometric volumetric methods specific to individual components (Harvey, 2000). The study of the properties of finished products was carried out by independent certificated laboratories according to standard methods approved by Ukrainian standards.

The ecological impact of waste storage facilities on the environment was investigated by analyzing hydrological and geological information from existing and accessible databases. A comprehensive approach and statistical data processing were used for the analysis.

Results & Discussion

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, Popasnyan district, on the site of the former Loskutiv stone quarry. 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 these is 375,268,749 tons. Some of them had ceased production.

As evidenced by the studies (I Nikolayeva et al., 2021), the landfill poses a fire, chemical, and environmental threat. The location of landfill site is located in the area of the folded Donbas, in the area of the so-called open carbon in the area of fine folding. Among the danger factors associated with the features of the geological environment of the site of the landfill, it is possible to mention the development of dangerous geological processes associated with its location in the zone of major tectonic disturbances, as well as the presence of conditionally unprotected underground aquifers, which are used as sources of local water supply.

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.

More than 100 types of industrial waste are stored in a landfill. A fairly large part of this list consists of spent catalysts. The landfill contains not only catalysts used at PJSC "Severodonetsk Azot", but also catalysts and metal-containing waste from other enterprises in the region are stored there. The waste contains vanadium, copper, nickel, cobalt, molybdenum, and platinum group metals.

The landfill of PJSC Severodonetsk AZOT has been in operation since 1968. The amount of waste entering the landfill is about 8-10 thousand tons/year. The waste depositor of PJSC Severodonetsk Azot is located in an area of 11 hectares and consists of 10 cards (Fig.1). All 10 maps of the solid industrial waste storage have one constructive solution: 4 m deep and 59x101 m in size, the bottom and slopes are lined with prefabricated reinforced concrete slabs.

The site of landfill is located in the area of the folded Donbas in the area of fine folding. The geological structure of the territory includes sedimentary rocks of the Carboniferous and Paleogene systems, covered from the surface by Quaternary sediments of insignificant thickness. Sandstones and limestone of the Gorlovskaya suite of the Carboniferous system with interlayers of argillites and siltstones lie under the area of the bottom of the reservoir. The rocks that make up the area form a brachyantclinal uplift cut in the northeast direction by the Maryiinsky thrust. The described dome structure is torn by numerous resets and thrusts in both sublatitudinal and submeridional directions. The central part of the storage area from the northeast to the southeast is crossed by a tectonic fault. Rocks, which are located in the block between this fault and the Maryiinsky thrust, have steep dip angles - up to 75° and more, while in the rest of the structure, the rock dip angle is 25-30°.

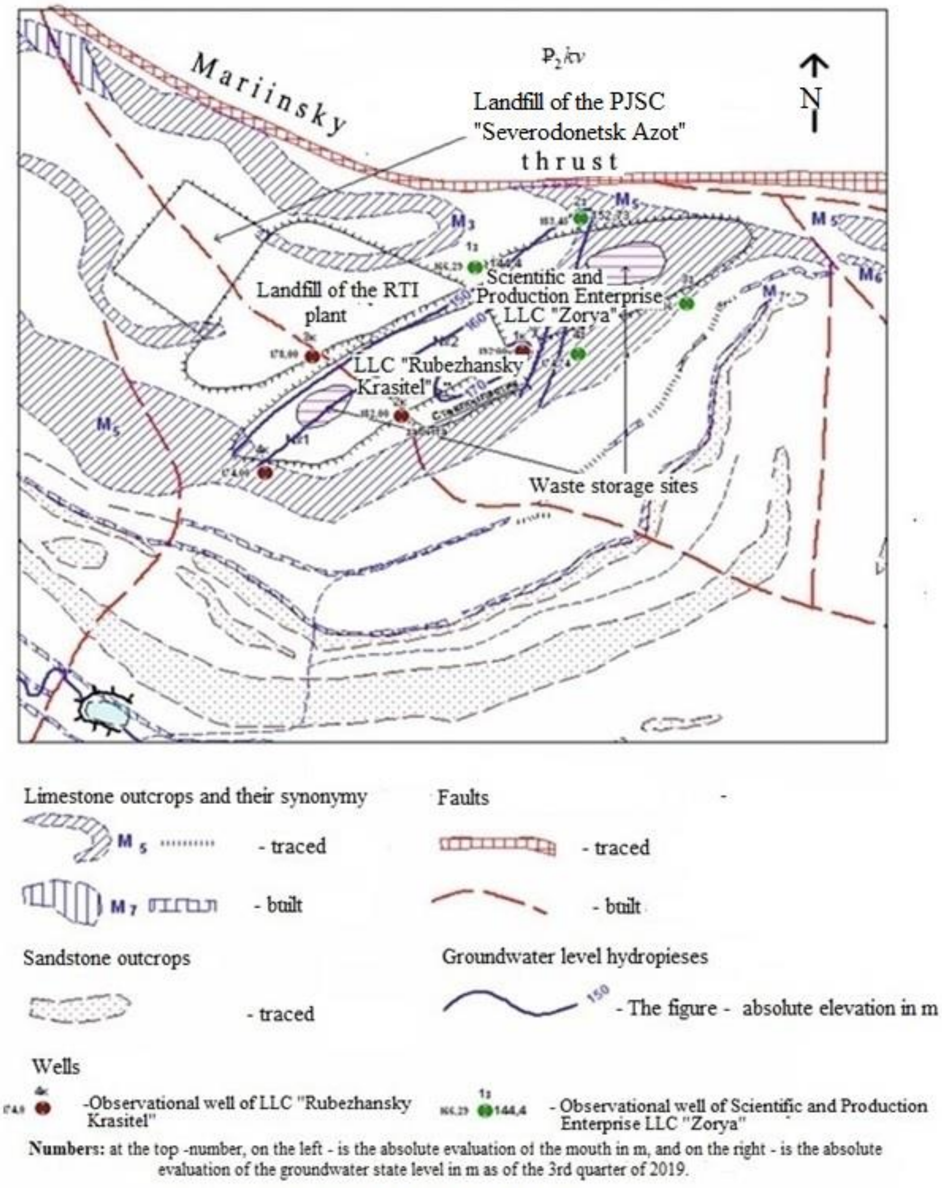

Fig. 1 The map of industrial waste disposal site

In addition, the hydrological conditions of the landfill site are characterized by the presence of an aquifer complex with a capacity of 15 to 20 m. The described aquifer complex has a very varied chemical composition: in the area of influence of the accumulator, underground waters are mainly chloride-sulfate magnesium-sodium and bicarbonate-chloride-sulfate magnesium-nitrite, on the area of influence – bicarbonate-chloride-sulfate calcium-magnesium-sodium and bicarbonate-sulfate-chloride sodium-magnesium.

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.

Of course, not all waste is acceptable in terms of ease of recycling, depending on a number of reasons and characteristics of the waste.

For instance, spent catalysts are convenient for processing, and their advantages for recycling are stability of the composition, limited number of containing components, simplicity of storage, and transportation. However, the stability of the composition is also a characteristic feature of some other wastes, including sludges from water treatment and wastewater treatment from metal impurities. An approximate list of components of spent catalysts and sludges is presented in Table 1.

The amount of generated spent catalysts depends on their service life and the size of the equipment. Typically, the service life (Scott, 2018) of catalysts ranges from several months to several years. But for more than 50 years of operation of the industrial waste landfill, their number is already quite large. The approximate amount of waste is indicated in the regional reports of the Department of Ecology and Natural Resources and the registers created by this organization.

Unfortunately, the open information is quite concise and does not contain all the necessary data to make a decision on the choice of disposal method. However, some information about the chemical composition of the waste can be obtained from the registry using the names of the processes and the catalysts used to carry out those processes.

Thus, in accordance with the information from the above-mentioned register, information is determined about spent catalysts stored at the sites of individual enterprises: for example, spent catalysts of the hydrogenation process of natural gas during the production of ammonia are stored at a landfill, mainly aluminum-cobalt-molybdenum with the content of the components CoO-2-6%, MoO_3 10-16%.

Table 1. 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,

More precisely, unfortunately, it is impossible to find out the chemical composition, because the suppliers of catalysts during the entire existence of the landfill are unknown. 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.

Many researchers were engaged in the processing of catalysts with the aim of extracting the most expensive and valuable components, offering mostly hydrometallurgical method (Sittig, 1980) as a series of successive leaching and precipitation operations, and it is also possible to use processes of ion exchange and electrochemical purification.

One of the wastes that have advantages similar to catalysts is water treatment waste. Usually, water treatment is a stable process, because the composition of water and waste from its preparation for industrial use depends mainly only on seasonal fluctuations.

For example, the water treatment waste of Severodonetsk Azot PJSC has a constant composition and contains components, the average composition was presented in the work (Korchuganova et al., 2018). 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. For obtaining calcium carbonate and calcium nitrate, the scheme shown in Fig. 2 is proposed.

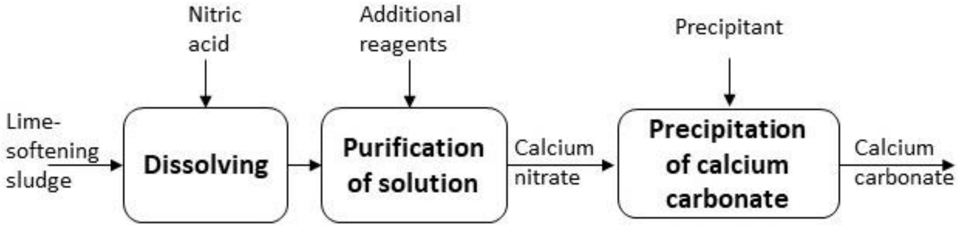

Fig. 2 The proposed scheme of water treatment waste processing

The resulting calcium nitrate solution was analyzed by an independent laboratory according to Ukrainian and EU standards, and the content of heavy metals and toxic components was not detected.

Calcium carbonate was obtained from a solution of calcium nitrate using urea and a more usual precipitant – a saturated solution of sodium carbonate. The sediments were analyzed by XRD and SEM analysis. According to the results of the XRD analysis, all the obtained samples have a crystal modification as calcite and similar crystallite sizes. The SEM results are presented in Fig. 3

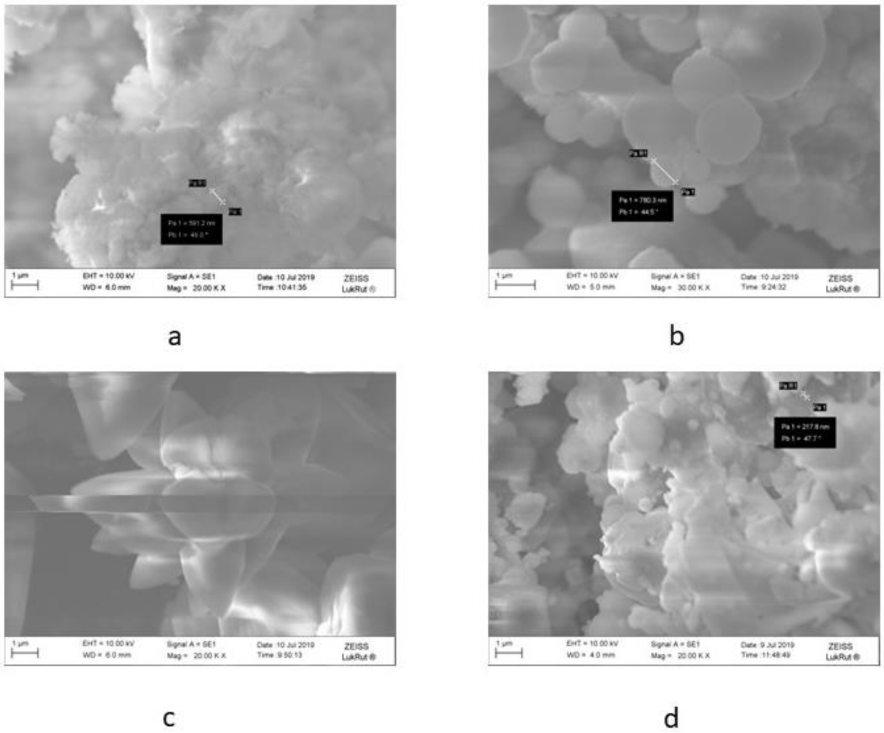

Fig. 3. SEM images of a) water treatment waste; b) calcium carbonate obtained by precipitation of sodium carbonate; c) calcium carbonate obtained by precipitation with urea; e) calcium carbonate obtained by a mixed method.

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.

Similar processes can be used for the disposal of sediments formed during the purification of wastewater from electroplating shops and water treatment waste. The reduction of capital investments in waste processing, especially at the stage of design and creation of processing technologies, could be helped by the creation of a database of technologies for their utilization, which would include data on the leaching kinetics of individual waste components.

In general, waste processing can be characterized as a sequence of technological operations for extracting valuable components. Most processes consist of dissolution and precipitation. Of course, each of the processes is related to the study of the nature of substances and the conditions under which the process must be carried out.

In general, each technological stage can be described by a system of equations. The mathematical model of the chemical process in this case consists of a system of kinetic and balance equations, the solution of which will allow to calculate of the composition of the reaction mixture at any moment of time, to conduct a preliminary assessment of the possibility of obtaining the desired product.

$$\begin{cases} m_i^{sol} = \alpha_i * m_i^{waste} \\ \alpha_i = F(C, \tau, T\ldots) \\ m_j^{sol} = \alpha_j * m_j^{\mathrm{waste}} \\ \alpha_j = F(C, \tau, T\ldots) \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ m_n^{sol} = \alpha_n * m_n^{\mathrm{waste}} \\ \alpha_n = F(C, \tau, T\ldots) \end{cases}$$

$m_{i,j,\ldots n}^{sol}$- the amount of component i, j...n that was extracted into the solution;

$m_{i,j,\ldots n}^{waste}$ - the amount of component i, j...n contained in the waste;

$\alpha_{i,j,\ldots n}$ is the degree of extraction of the reagent from waste.

$F(C,\tau,T)$ – kinetic and balance equations that allow you to calculate the degree of extraction of individual waste components.

Mathematical equations describing individual processes are usually obtained by scientists of various specialties during research.

$$\alpha_n = F(C, \tau, T\ldots)$$

Equations have a different form, reduced to the conditions of the problem to be solved. Information on the dissolution of metal compounds and individual reactions in water, solutions of acids, and alkalis are of a scattered nature. They are not systematized and not accumulated. As a rule, there is no exchange of received data between researchers working in different fields of science, which leads to some duplication of research. The systematization of already obtained dependencies and their accumulation in a specialized database would allow us to quickly conduct preliminary calculations of the processes of extracting valuable components from raw materials. In turn, this will allow you to quickly choose a method of processing raw materials, and minimize the costs of cleaning the resulting product from impurities.

Another limitation of the use of waste is related to the possibility of obtaining products of commercial quality from it. Likely, the processing of spent catalysts into fresh ones does not always give a positive result due to the difficulty of extracting some impurities that reduce the catalytic activity of such materials. Obtaining nano-sized materials could help in solving such a problem. Particle size affects three main groups of properties of any material. Firstly, on structural characteristics (lattice symmetry and cell parameters), and secondly, on electronic properties of oxides. Structural and electronic properties determine the third group of properties: physical and chemical. Such a decision could one of the possibilities to compensate for the drop-in catalytic activity.

An experiment was conducted on the processing of spent aluminum-nickel catalyst, one of those stored at the industrial waste landfill. Processing was carried out according to the scheme shown in Fig. 4.

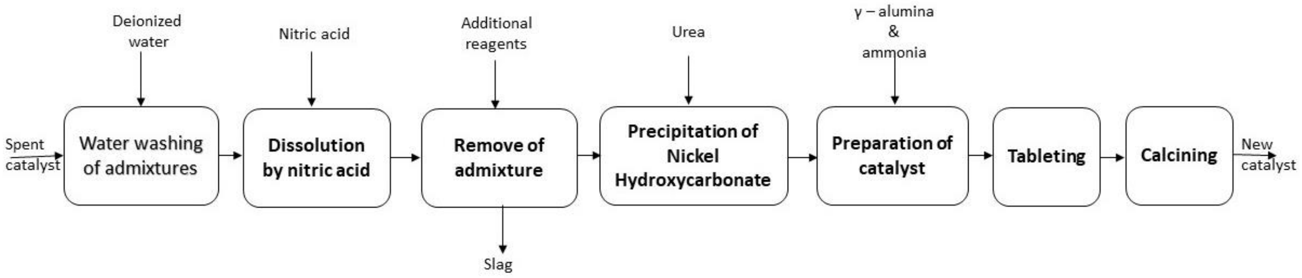

Fig. 4 Scheme of processing spent aluminum-nickel catalyst

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. From which samples of the catalyst were made (Korchuganova et al., 2020), its specific surface was measured, which turned out to be 22-24% greater than the surface of the sample prepared from industrial reagents.

Conclusion

Some waste stored at industrial landfills in the Luhansk region contains CRM, such as vanadium, magnesium, and precious metals. Depending on the origin of waste and storage conditions, the chemical composition may be different. Most of the waste that has a stable composition and good storage conditions can be processed into marketable products. This particularly applies to spent catalysts and water treatment waste.

Absolutely, before use, the waste stored at the landfill should be inventoried in detail, including storage conditions.

Among other things, there is the problem of recycling catalysts in the pharmaceutical industry (R et al., 2017), which can be solved by selecting dissolution and precipitation conditions.

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