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To cite this article: T Suponik et al 2018 IOP Conf. Ser.: Mater. Sci. Eng. 427 012040

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The testing of waste from the installation of salt debris leaching

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Abstract. Although the Salt Mine in Bochnia is designed for tourism, it still produces waste. In order to reduce the mass of waste and its harmful impact on the environment, the leaching method was proposed. The authors of the article have presented in their earlier works the method of leaching a salt debris as well as the large-scale laboratory installation used for leaching. The waste generated in the leaching installation are to be used e.g. for the production of building materials or, in the worst case, stored in landfill. The aim of the article was to assess the possibility of their storing at the landfill of inert waste or using them as a secondary raw material in the environmental aspects. The analysis of the mineral and chemical composition of salt debris and waste after leaching in the installation as well as the chemical composition of the leachate after the leaching tests of these waste were performed. Halite, anhydrite and gypsum are the dominant mineral in salt debris, whereas only anhydrite and gypsum in waste after leaching in a large-scale laboratory installation. The remaining, in smaller amounts, minerals are illite and quartz. Waste from the installation of salt debris leaching still release small amounts of chlorides into the water. Therefore waste still poses a threat to the environment. In order to reduce the amount of chlorides released into the environment, the pump in the leaching plant should work longer than the assumed 5 minutes or the leaching temperature should be higher than 15°C.

1. Introduction
The Bochnia Salt Mine produces large amounts of waste in the form of salt debris annually. This is to maintain tourist routes and create new underground heading elements. In the case of active mines, the debris are used in liquidation works [1].

The Salt Mine in Bochnia is not active, so there are no new locations to store salt debris. In order to reduce the mass of waste and its harmful impact on the environment, the leaching method in 2017 has been proposed. Pierzyna et al. presented in their paper [2] the method of leaching a salt debris as well as the large-scale laboratory installation used for leaching. The saturated brine and waste will be created as a result of this operation. In the article, this waste is called waste after leaching. Saturated brine is to be pumped into inactive underground excavations, salt caverns tightly isolated from groundwater, while the waste from the leaching installation either is to be used as a secondary raw material or disposed at a landfill for inert waste. This article answers the question about the possibility of such waste management, in the environmental aspects. Thus, the aim of the article is to assess the possibility of their storing at the landfill of inert waste or using them as a secondary raw material in the environmental aspect. The following studies were carried out:
- the analysis of mineral and chemical composition of salt debris and waste after leaching,
- the analysis of chemical composition of the leachate after the leaching test for both salt debris and waste after leaching,
- the analysis of weight loss during the roasting process of the salt debris and waste after leaching.

2. Material and methods
The waste for the environmental tests was obtained from the laboratory installation for waste leaching located at the technological hall of the Silesian University of Technology. The system operates as a closed cycle and is equipped with a PH65 Powen's rotary pump, which serves the mixing, pumping and exchange of the mixture in the tank. The piping is equipped with a series of flap valves allowing for the control of the flow through the selected diameters of the pipes [2]. The tests were conducted for one grain classes: 0-6 mm. The leaching temperature was set at 15°C, whereas thy leaching time was 5 minutes, according to previous research and recommendations presented in the article [2]. The waste was then dried.

In order to identify the mineral and chemical composition of the samples (salt debris and waste after leaching), the X-ray diffraction (XRD) method and X-ray fluorescence (XRF) were used, respectively. For the analysis of crystalline substances, AERIS 1 with a CuKα lamp by PANalytical was used. Working conditions of the diffractometer: voltage 40kV, current intensity 8 mA, the step of 0.003° of 20 angle, time 4.84 s, the range of the 20 angle 7-77°. The identification of elements and determination of atomic concentrations of samples were performed using Epsilon 1 Spectrometer by PANalytical.

A roasting was used to check the total weight loss of the samples at high temperature. The samples were comminuted and sieved to a size < 0.1 mm. Approximately 2 grams of both salt debris and waste after leaching were roasted for 3 hours in a laboratory furnace at 850°C. The temperature in the furnace increased to 500°C for 40 minutes and to 850°C for a further 20 minutes. Then the temperature was maintained at 850°C for 3 hours. The samples were weighed before and after roasting, and then the total weight loss was calculated as a percentage.

In order to assess the possibility of storing waste at the landfill of inert waste, according to the Regulation of the Minister of Economy [3], and their impact on the environment, the waste was leached in a ROTAX 6.8 shaker in accordance with the PN-EN standard [4]. The liquid/waste ratio (L/S) in the tests was 10:1, while the shaking time was 24 hours. The leaching test was carried out at 22°C. Determination of the content of chemical substances and parameters in the eluates formed during the leaching tests was performed using JY2000 spectrometer (ICP-AES) for elements, DR5000 UV-Vis spectrophotometer for chlorides, fluorides, sulfates, phenol indicator, Shimadzu TOC-V<sub>CSH</sub> Analyser and Shimadzu ASI-C sampler for dissolved organic carbon and Knick PORTAMESS meters for Total Dissolved Solids.

Four samples of salt debris and four samples of waste after leaching were taken for roasting and leaching tests, and the results were presented as an arithmetic average.

3. Results and discussion

3.1. X-ray diffraction (XRD)
Based on the diffraction patterns presented in figure 1 and 2 it can be noticed that the mineral composition of the samples, i.e. salt debris and waste after leaching, was practically the same. Both of the samples consist the following minerals:
- halides, represented by halite (NaCl) and sylvine (KCl),
- calcium sulphates, represented by anhydrite (CaSO<sub>4</sub>) and gypsum (CaSO<sub>4</sub>x2H<sub>2</sub>O),
- mineral from the silica group, represented by quartz (SiO<sub>2</sub>),
- clay minerals, represented by illite (K<sub>0.6-0.85</sub>Al<sub>2</sub>(Si,Al)<sub>4</sub>O<sub>10</sub>(OH))<sub>2</sub>.
This was indicated by the characteristic reflections from these minerals, appearing on the diffraction patterns (figures 1 and 2).

- halite: 3.25, 2.82, 1.99, 1.70, 1.63, 1.41, 1.26Å,
- anhydrite: 3.88, 3.50, 3.12-3.11, 2.85, 2.47, 2.33, 2.21, 2.18, 2.08, 1.94, 1.87, 1.75, 1.65, 1.56, 1.52, 1.49Å,
- gypsum: 7.62-7.60, 4.28, 3.06, 2.68Å,
- quartz: 4.25, 3.34, 2.46, 2.28, 2.13, 1.81, 1.54Å,
- illite: 10.21-10.19, 4.47-4.46, 2.36Å,
- sylvine: 3.11, 2.89, 2.20, 2.04, 1.29Å.

The intensity of basic reflections indicated a clear quantitative differentiation of minerals in the samples:

- in salt debris the halite and anhydrite dominated, while illite, quartz and sylvine were identified in smaller quantities,
- in the waste after leaching anhydrite prevailed, but there were also, in much smaller quantities, illite, quartz, halite and sylvine.

![Figure 1. Diffractogram for the salt debris. A – anhydrite, G – gypsum, H – halite, I – illite, Q – quartz, S – sylvine.](image-url)
3.2. X-ray fluorescence (XRF)

The results of the tests using XRF spectrometer are presented in table 1. These results show that the chemical composition of both samples differs significantly:

- in salt debris Na$_2$O and Cl dominated, with contents of 22.65 and 26.48 % by mass, respectively. There were also SiO$_2$, CaO and SO$_3$, in an amount of over ten percent each,
- in waste after leaching there were SO$_3$ and CaO, together in an amount of over 89 % by mass.

The other chemical components were present in much smaller quantities.
Table 1. Chemical composition of the tested samples (in % by mass).

| Chemical ingredient | The name of the sample       |
|---------------------|-----------------------------|
|                     | Salt debris | Waste after leaching |
| SiO$_2$             | 15.08       | 5.84              |
| TiO$_2$             | 0.25        | 0.03              |
| Al$_2$O$_3$         | 5.32        | 2.09              |
| Fe$_2$O$_3$         | 1.83        | 0.26              |
| CaO                 | 13.09       | 37.15             |
| Na$_2$O             | 22.65       | 1.11              |
| K$_2$O              | 1.22        | 0.13              |
| SO$_3$              | 14.05       | 52.03             |
| Cl                  | 26.48       | 1.35              |
| V$_2$O$_5$          | 0.01        | 0.00              |
| Cr$_2$O$_3$         | 0.01        | 0.00              |
| MnO                 | 0.03        | 0.00              |
| CuO                 | 0.01        | 0.00              |
| SUMA                | 100.00      | 100.00            |

Based of mineral and chemical composition the percentage of mineral components in both samples was calculated (anhydrite and gypsum were presented together as calcium sulphates). The results were presented graphically in the figure 3.

In salt debris, the dominant mineral was halite in the amount of 47% by mass, while the second component was calcium sulphate in the amount of 26% by mass (see figure 3). The content of illite and quartz was very similar and amounted to 12-13% by mass, while the content of sylvine was 2% by mass.

In the waste after leaching calcium sulphates (anhydrite and gypsum) were dominated (nearly 90% by mass). The content of the remaining minerals were: quartz and illite 4% by mass each, halite 2% by mass and sylvine 1% by mass.

![Figure 3. The content of mineral components in the tested samples.](image)
3.3. Weight loss during roasting
The weight loss of samples as a result of roasting at 850°C, for salt debris and waste after leaching, was 1.6365 % and 0.3718 %, respectively. The loss of mass is much smaller (more than four times) for waste after leaching. This indicates that this material contains less minerals that undergo chemical changes that cause the loss of mass due to high temperature. Gypsum and especially anhydrite, which together make up 89% of the total, belongs to such minerals. As a result of raising the temperature to 150°C, the gypsum turns into burned gypsum, and up to 200°C in anhydrite. These changes cause loss of water from the sample, thereby reducing its weight to a small extent. At temperatures up to 850°C (and even up to 1180°C), the anhydrite changes slightly, which does not lead to weight loss [5].

3.4. Leaching tests
Based on the results of leaching tests (table 2), it can be claimed that waste from the installation of salt debris leaching can be stored in the landfill of waste other than hazardous and inert, according to the Regulation of the Minister of Economy [3]. Chlorides are the only substance that exceeds the permissible values of their storage at landfills for inert waste. The test results indicate elevated concentrations of copper and zinc in the eluates. These values, however, do not exceed the permissible level, according to the Regulation of the Minister of Economy, for both types of landfills. Based on these observations, it is recommended that the pump in the leaching plant should work longer than the assumed 5 minutes or the leaching temperature should be higher than 15°C. If one or both of these conditions are met, the waste may be stored at the landfills of inert waste and will not be a problem for the environment. At the same time, it can be expected that the waste will be able to be used in engineering works (e.g. in the production of building materials). For this purpose, however, additional studies needs to be done.

In order to obtain a product with a high content of calcium sulphate and a suitable crystalline structure the waste should be free of impurities [5]. Then the waste can be thermally treated. Directions for the use of waste containing a very large amount of calcium sulphate have been presented in the following papers [6,7].
Table 2. The results of the leaching tests of waste vs the permissible values of substance/parameters that allow to storage them at the landfills of inert waste or at the landfills of waste other than hazardous and inert, in mg/kg of dry matter; L/S = 10 dm$^3$:1 kg.

| Substance/parameter | The results of leaching tests for: | The permissible values* of substance/parameters that allow to storage waste at the landfills of: |
|---------------------|-----------------------------------|-------------------------------------------------------------------------------------------------|
|                     | salt debris | waste obtained from the installation of salt debris leaching | inert waste | waste other than hazardous and inert |
| Arsenic (As)        | <0.04       | <0.04                                                       | 0.5        | 2                                    |
| Barium (Ba)         | 7.11        | 1.94                                                       | 20         | 100                                  |
| Cadmium (Cd)        | 0.24        | <0.002                                                     | 0.04       | 1                                    |
| Chromium tot. (Cr)  | 2.90        | 0.05                                                       | 0.5        | 10                                   |
| Copper (Cu)         | 12.44       | 1.35                                                       | 2          | 50                                   |
| Mercury(Hg)         | 0.04        | <0.002                                                     | 0.01       | 0.2                                  |
| Molybdenum (Mo)     | 0.14        | <0.006                                                     | 0.5        | 10                                   |
| Nickel (Ni)         | 4.45        | 0.09                                                       | 0.4        | 10                                   |
| Lead (Pb)           | 3.81        | <0.03                                                     | 0.5        | 10                                   |
| Antimony (Sb)       | <0.01       | <0.01                                                     | 0.06       | 0.7                                  |
| Selenium (Se)       | <0.02       | <0.02                                                     | 0.1        | 0.5                                  |
| Zinc (Zn)           | 9.24        | 0.6                                                       | 4          | 50                                   |
| Chlorides (Cl$^-$)  | 307 646     | 7160                                                      | 800        | 15 000                               |
| Fluorides (F$^-$)   | 1.21        | <0.02                                                     | 10         | 150                                  |
| Sulphates (SO$^{4-}$)| 1 084       | 459                                                       | 1000       | 20 000                               |
| Phenol indicator    | <0.1        | <0.1                                                     | 1          | -                                    |
| Dissolved organic carbon | 15      | 2                                                         | 500        | 800                                  |
| Total dissolved solids | >19990   | 14 225                                                    | 4000       | 60 000                               |

* - according to the Regulation of the Minister of Economy [3]

4. Conclusions

- The salt debris from the Salt Mine in Bochnia, which has not undergone any processes, releases to the aquatic environment chlorides, sulphates as well as chromium, copper, nickel, lead and zinc in ionic state, while waste from the installation of salt debris leaching only chlorides. Extending the leaching time in the leaching installation and/or increasing the process temperature (both factors to a small extent) will improve the efficiency of the process and will make the waste environment-friendly.

- The salt debris mainly consists of halite, anhydrite and gypsum, illite and quartz, while waste from leaching installation from anhydrite and gypsum. The latter material could be used, after prior preparation, for the production of building materials.

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