

# Extraction of Vanadium from the Dust of Ore-Thermal Melting of Ilmenite Concentrate Using Deep Eutectic Solvents

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During the production of titanium slag by melting ilmenite concentrate, a large amount of dust is formed, most of which is taken to the landfill. The problem of dust disposal and recycling is the most important task of titanium production, since valuable components that can be extracted are lost along with the dust. In addition, the storage of dust in open landfills causes great harm to the environment. The use of deep eutectic solvents as green solvents for dust leaching has great prospects. The possibility of extracting vanadium from the dust of ore-thermal melting using deep eutectic solvents based on choline chloride and carboxylic acids is investigated. The highest yield of vanadium was during leaching in the Oxaline system and amounted to 89 %. The results of leaching were compared with leaching with equivalent aqueous acid solutions. The effect of ultrasound on the time of the leaching process was also studied. The resulting vanadium-containing material can be used as an additive to the charge in the accompanying technology for the production of vanadium pentoxide.

## 1. Introduction

The production of titanium slag is carried out by reducing the melting of ilmenite concentrate in an ore-thermal furnace. During the melting process, titanium slag, associated metal and waste gases are formed. The waste gases are deposited in the dust collecting chamber and captured in cyclones and bag filters. Coarse dust is captured in cyclones, and fine dust is captured in bag filters. The composition of the dust depends on the composition of the charge, the operating mode, temperature and time from the beginning of melting to the end of the cycle. The resulting dust consists of oxides of titanium, iron, zinc, manganese, silicon, as well as a small amount of rare, scattered and radioactive metals. The problem of utilization of ore-thermal melting dust is associated with the presence of lead and polonium radionuclides in it. The accumulation of dust in landfills causes serious damage to the environment. Vanadium, iron and aluminum are harmful impurities for titanium slag, since they complicate the subsequent chlorination process (Garmata et al., 1983). Consequently, the utilization of ore-thermal melting dust is relevant for titanium production enterprises. In the modern world, at most enterprises producing titanium slag from ilmenite concentrate by ore-thermal melting, the captured dust is sent back to the smelter, mixing it with the charge. At the same time, depending on the composition of the charge, the dust additive should not exceed 10 % of the mass of the charge.

For example, PJSC "VSMPO-AVISMA" Corporation (Russian Federation) operates a fine gas purification plant that reduces solid emissions into the atmosphere from 50 t to 100 kg/month. Some of the captured dust is returned to production, the other part is stored in landfills. To remove dust, a method for adding granular dust to titanium slag for chlorination is proposed (Teterin et al., 2019). But this involves solving additional tasks to ensure the required purity of titanium tetrachloride.

The titanium industry of Kazakhstan is represented by JSC "Ust-Kamenogorsk titanium and magnesium plant". JSC "UK TMP" manages the technological chain of titanium production from ilmenite concentrate to titanium ingots and alloys. At the stage of ore-thermal melting of ilmenite concentrate, about 120 t of dust are exported to landfills annually. The proposed method of utilization of ore-thermal melting dust has two main advantages: the use of environmentally friendly solvents and the extraction of valuable components.

In this study, we investigate an ionometallurgical approach to the leaching of dust from the ore-thermal melting of ilmenite concentrate using four different types of deep eutectic solvents for the selective extraction of target metals from the base material.

The discovery of deep eutectic solvents (DES) was a major breakthrough in the world of green chemistry. Deep eutectic solvents are often defined as binary or ternary mixtures of compounds that are able to bind mainly using hydrogen bonds. The combination of these compounds in a certain molar ratio leads to the formation of a eutectic mixture (Zhang et al., 2012). Deep eutectic solvents are used worldwide in a wide range—from the manufacture of medicines to ion metallurgy. DES have a unique combination of physical and chemical properties, which makes them very attractive for metal processing, organic synthesis, biodiesel purification, and catalysis (Smith et al., 2014). They consist of a eutectic mixture of at least two compounds, namely a hydrogen bond acceptor (for example, quaternary ammonium halide salts, metal chlorides, etc.) and a hydrogen bond donor (for example, carboxylic acids, amides, alcohols, etc.), and may consist of various cationic and anionic varieties. Abbott et al. (2004) investigated deep eutectic solvents based on choline chloride and carboxylic acids, their physicochemical properties, and compared them with ionic liquids. Later, the solubility of 17 widely used metal oxides in choline chloride-based DES was investigated (Abbott et al., 2006). The ability to selectively extract metals from the oxide matrix made it possible to use DES for processing industrial waste. Abbott et al. (2009) described the design and operation of the first large-scale extraction and separation of metals from a complex dust matrix of electric arc furnaces using an ionic liquid. Bakkar (2014) also investigated the possibility of processing electric arc furnace dust. Bakkar and Neubert (2019) showed the utilization of the dust of the wagons with the extraction of zinc. Thus, the extraction of various metals from the oxide dust of zinc production using DES was previously investigated. However, the possibility of using DES in the processing of titanium dust has not been investigated. Also, when leaching dust, mechanical mixing was always used, while the duration of the process reached 48 h. For the first time, the use of ultrasound when working with DES was carried out by Singh et al. (2012), when they performed work on the synthesis of new oxazole compounds. The use of ultrasound effectively affects the reaction speed and reduces the process time.

The purpose of this study is to obtain a vanadium-containing material from the dust of titanium production using DES based on choline chloride and carboxylic acids. The optimal process parameters and the yield of the target components were determined during a 24 h dust leaching. The results were compared with the results of leaching with equivalent aqueous solutions of carboxylic acids. The efficiency of the leaching process during mechanical mixing and mixing using ultrasound is also compared. The possibility of using the obtained vanadium-containing pulp as an additive in the processing of pulp of cubic residues of distillation columns is shown.

## 2. Experimental procedures

Choline chloride (> 99 %) was purchased from Sigma Aldrich (Germany), oxalic acid (> 99 %), succinic acid (> 99 %), ethylene glycol (> 99 %), and urea (> 99 %) were purchased from Cris Analit, Kazakhstan.

All chemicals had low trace metal contents and were used as received without further purification. DES components were dried under vacuum at a temperature of 120 °C. Then they were mixed in the appropriate molar ratio, as shown in Table 1, where HBA is a hydrogen bond acceptor, HBD is a hydrogen bond donor.

*Table 1: Used deep eutectic solvents based on choline chloride formed at the specified HBA: HBD ratios*

HBA	Molar ratio	HBD
Choline chloride	1:2	ethylene glycol
	1:2	urea
	1:1	oxalic acid
	1:1	succinic acid

The mixture was heated to 80 °C and stirred for 6 h until a colourless homogeneous liquid was formed. The water content in pure DES was determined using a Karl Fischer C 20 coulometric titrator (Mettler Toledo).

The dust of ore-thermal melting of ilmenite concentrate was taken from the dumps of JSC "UK TMP". The dust was crushed using a planetary ball mill (FRITSCH PULVERISSETTE 7), working with a grinding cup made of yttrium-stabilized zirconium oxide. The dust portions were dried at 150 °C for 12 h until the mass remained constant. On average, the weight decreased by 12 %. Analysis of liquid and solid samples were carried out using the following analytical techniques: XRF, ICP-OES, ICP-MS, XRPD. The following instruments were used: D8 Advance diffractometer ("BRUKER"),  $\alpha$ -Cu radiation; Agilent 4100 microwave plasma atomic emission spectrometer; Agilent 7500cx ICP-MS inductively coupled plasma mass spectrometer ("Agilent Technologies"); X'Pert PRO diffractometer ("PANalytical"). Leaching was carried out by mechanical stirring using a magnetic

stirrer and an ultrasonic bath UC-4120. Leaching experiments were performed at 70 °C using a leach volume of 50 mL to 200 mL and a liquid-solid ratio (L/S) of 10. The quantitative composition of dust using XRF, ICP-OES, and ICP-MS is presented in Table 2.

Table 2: Main components of ore-thermal melting dust

Element	mg / kg
Ti	278,290
Fe	178,940
Mn	12,540
Pb	8,453
Zn	45,410
Si	27,310
V	2,148

The appearance of the ore-thermal melting dust is shown in Figure 1.



Figure 1: Appearance of ilmenite concentrate ore-thermal melting dust

The results of X-ray phase analysis of ore-thermal melting dust are presented in Table 3.

Table 3: X-ray phase composition of ore-thermal melting dust

Compound Name	Formula	S-Q
Rutile, syn	Ti <sub>0.992</sub> O <sub>2</sub>	29.1 %
Ilmenite, syn	FeTiO <sub>3</sub>	20.8 %
Diiron (III) titanate / Iron Titanium Oxide	Fe <sub>2</sub> TiO <sub>5</sub>	16.8 %
Quartz, syn	SiO <sub>2</sub>	13.0 %
Rutile	TiO <sub>2</sub>	7.7 %
Hematite, syn	Fe <sub>2</sub> O <sub>3</sub>	6.1 %
Chromium Iron Oxide	FeCrO <sub>3</sub>	5.4 %
Manganese Iron Oxide	Mn <sub>1.58</sub> Fe <sub>1.42</sub> O <sub>4</sub>	1.0 %

To study the leaching behavior and identify trends in selectivity, the dust was leached in 4 small (V = 50 mL) DESs for 10 h at a temperature of 70 °C. The results are compared in Table 4.

Table 4: Leaching yields using different DESs

DES	Leaching yield ( % )						
	Ti	V	Fe	Mn	Pb	Zn	Si
ChCl + ethylene glycol	< 0.001	> 0.01	> 0.01	0.95	0.18	0.019	0.32
ChCl + urea	< 0.001	0.016	> 0.01	0.45	0.12	> 0.01	0.56
ChCl + oxalic acid	0.14	66.2	2.2	9.0	1.47	10.1	32.5
ChCl + succinic acid	2.1	38.2	2.6	6.1	2.0	4.8	44.2

Leaching was carried out at a temperature of 70 °C, since the viscosity of the solution increased at a temperature below 50 °C, and when the temperature rose above 80 °C, DES slowly decomposed. The ratio of liquid to solid (L/S) is from 10 to 20. With a decrease of < 10, the viscosity increases significantly and the filtration rate decreases, and with an increase of > 20, an unjustified overspending of the solvent occurs. The leaching experiments were carried out at 70 °C using a leaching volume of 75 mL to 200 mL and a liquid/solid ratio (L/S) of 10. Samples with a volume of 5 to 10 mL were taken after a certain reaction time, filtered at the appropriate leaching temperature, and then diluted for ICP-OES and analysis using aqueous solutions of HNO<sub>3</sub> and HCl.

### 3 Results and discussion

Ethylene and Relin showed low efficiency of dust leaching. The highest yield was in silicon. DES based on carboxylic acids showed high yields of target metals. As expected, the oxide dust is easily dissolved by the much more acidic oxaline. In addition, it is known that oxalate is a good ligand for many cations of divalent and trivalent metals. In conclusion, it should be noted that the most promising candidates for the extraction of the target metal were deep eutectic solvents with oxalic and succinic acids. Therefore, further experiments were focused on the leaching of dust in these DES.

#### 3.1 Investigation of the yield of target metals during leaching with deep eutectic solvents with succinic and oxalic acids

Leaching was carried out by mechanical stirring for 24 h. Graphs of the dependence of the yields of the target metals on the leaching time are shown in Figure 2.

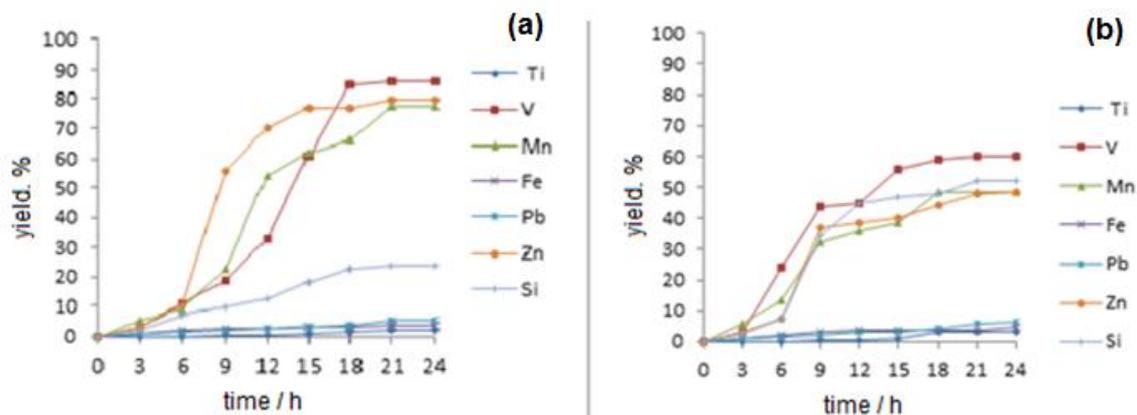


Figure 2: Yields of the process relevant metals for 24 h leaching experiments of dust in Oxaline (a) and (ChCl + succinic acid) system (b) at 70 °C with a L/S ratio of 10

As can be seen from the graphs, the dissolution of metals in the solvent begins actively with 6 h of leaching. For oxaline, high yields of vanadium, manganese and zinc are noticeable, and silicon also passes into the solution by 25 %, which complicates filtration. The yields of titanium, iron, and lead do not exceed 10 %. In DES with succinic acid, the leaching process starts faster, but the yields of the target metals are lower than in the oxalin system. And the high extraction of silicon makes the filtration process very difficult.

#### 3.2 Investigation of the yields of target metals during dust leaching using aqueous solutions of carboxylic acids

Figure 3 shows the results of dust leaching with aqueous solutions of oxalic and succinic acid. Experiments were conducted with acid concentrations of 60 g/L and 90 g/L. The highest yields were shown by acids with a higher concentration. However, in comparison with the corresponding DES, the yields for the target metals are significantly lower. Thus, in oxalic acid, the yield of vanadium, manganese and zinc does not exceed 45 %. In succinic acid, the yield of zinc was 65 %, and vanadium, manganese did not exceed 35 %.

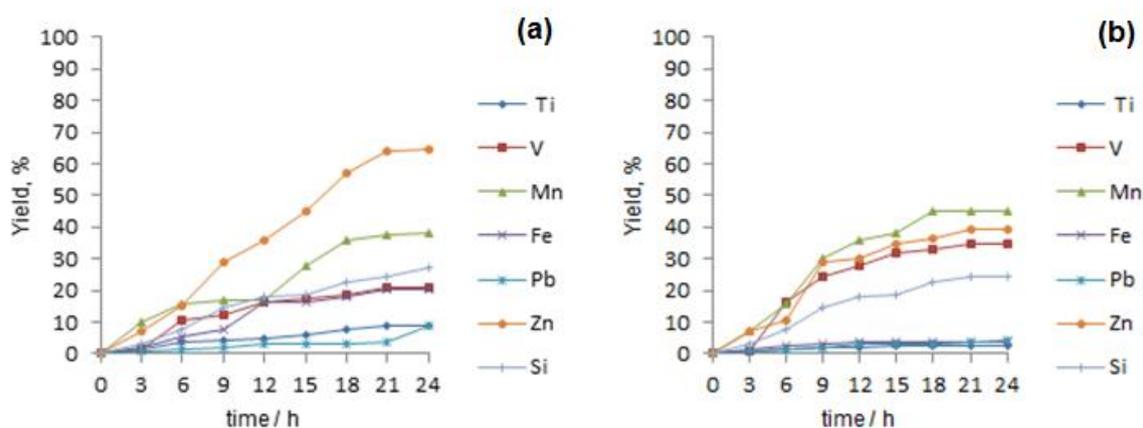


Figure 3: Comparison of 24 h dust leaching experiments using 90 g/L oxalic acid, (a) and succinic acid; (b) at 70 °C with a L/S ratio of 10

### 3.3 Investigation of the yields of target metals during leaching using ultrasound

To speed up the process, an ultrasonic bath was used. The temperature was maintained at 70 °C with a L/S ratio of 10. Graphs of metal yields when using ultrasound are shown in Figure 4.

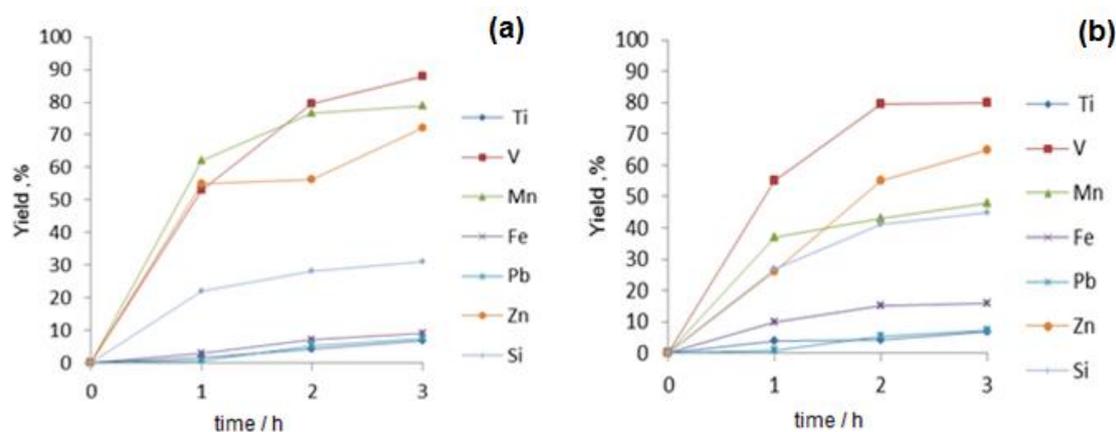


Figure 4: Comparison of 3 h leaching experiments of dust in Oxaline (a) and (ChCl + succinic acid) system (b) at 70 °C with a L/S ratio of 10 using ultrasound

After 1 h, there is an increase in the yields of vanadium, manganese and zinc up to 60 % and silicon up to 30 % in the oxaline system. After 3 h, the vanadium yield was 88 %, and the manganese and zinc yield was almost 80 %. The yield of silicon reached 30 %. In the (ChCl + succinic acid) systems and after the first hour there was a noticeable increase in yields. The vanadium yield was 55 %, manganese and zinc about 37 % and 26 %. After 1 h the yield of iron increased to 10 %, titanium to 4 %, and silicon to 40 %. This may be due to the dissolution of iron titanate and ilmenite. With further leaching, a decrease in metal yields was observed due to the destruction of the organic solvent.

### 3.4 Use of vanadium-containing pulp

The resulting solution after leaching is thickened and evaporated to obtain a vanadium-containing pulp. The technology of processing the pulp of the cubic residues of distillation columns is based on the sequential chlorine-thermal separation of titanium tetrachloride and vanadium oxytrichloride from them. For the production of vanadium pentoxide, the pulp of the cubic residues of distillation columns is used as a raw material. The pulp of the cubic remains of rectification columns consists of titanium tetrachloride with suspended particles of vanadium oxychlorides, titanium trichlorides, aluminum and iron. Vanadium pentoxide is obtained from technical vanadium oxytrichloride by extraction technology.

The requirements for the content of vanadium in the supplied grades of pulp of cubic residues are presented in Table 5.

*Table 5: The required composition of the pulp of the cubic residues of the distillation columns*

Name of indicators	Standards for grade	
	Grade 1	Grade 2
Vanadium,%, not less	0.85	0.50
Solid suspensions, g/L, not more than	200	200

#### 4. Conclusions

Four different DESs were investigated for the leaching and selective extraction of vanadium and other metals from oxide dust and compared with experiments in an aqueous solution of oxalic and succinic acids. DES with oxalic succinic acid were recognized as the most effective leaching agents. The raw material consisted of rutile, ilmenite, and iron titanate as the main crystalline phase, as well as iron oxide of manganese, hematite, and quartz. High yields of manganese, vanadium, and iron indicate the dissolution of manganese oxide and iron titanate. The titanium contained in the rutile practically did not dissolve. The yield of vanadium was 89 %, manganese 77 % and zinc 79 % for DES with oxalic acid. The yield of vanadium was 60 %, of manganese and zinc-up to 50 % for DES with succinic acid. Silicon leaching significantly reduces the filtration rate. Titanium and iron mostly pass into the sediment. The results of leaching with aqueous acid solutions were compared. Leaching using DES showed the best results in the yield of target metals. The use of ultrasound reduces the time of the leaching process and increases the yield of target metals. After 3 h of ultrasound leaching, the yields of the target metals were higher than after 48 h of leaching with mechanical stirring.

The resulting vanadium-containing material meets the requirements for raw materials for the production of vanadium pentoxide according to the technology used at JSC "UK TMP". A promising direction may be the development of a technology for separating vanadium and other metals from the resulting solution and its subsequent regeneration in order to create a closed cycle.

#### References

- Abbott A. P., Boothby D., Capper G., Davies D. L., Rasheed R. K., 2004, Deep Eutectic Solvents Formed between Choline Chloride and Carboxylic Acids: Versatile Alternatives to Ionic Liquids. *Journal American Chemical Soc.*, 126, 9142–9147.
- Abbott A. P., Capper G., Davies D. L., McKenzie K. J., Obi S. U., 2006, Solubility of Metal Oxides in Deep Eutectic Solvents Based on Choline Chloride. *J. Chemical Engineering*, 51, 1280–1282.
- Abbott A. P., Harris R. C., Frisch G., Hartley J., Holyoak F., Jenkin G. R., 2015, Electrocatalytic Recovery of Elements from Complex Mixtures using Deep Eutectic Solvents. *Green Chem.*, 17, 2172– 2179.
- Abbott A. P., Frisch G., Hartley J., Ryder K. S., 2011, Processing of metals and metal oxides using ionic liquids. *Green Chem.*, 13, 471–481.
- Bakkar A., 2014, Recycling of electric arc furnace dust through dissolution in deep eutectic ionic liquids and electrowinning. *Journal of Hazardous Mater.*, 280, 191–199.
- Bakkar A., Neubert V., 2019, Recycling of cupola furnace dust: Extraction and electrodeposition of zinc in deep eutectic solvents. *Journal Alloys Compd.*, 771, 424–432.
- Garmata V. A., Petrunko A. N., Olesov U. G., Sandler R. A., 1983, *Titanium*. Moscow, USSR, Metallurgy, 554.
- Singh B. S., Lobo H. R., Pinjari D. V., Jarag K. J., Pandit A. B., Shankarling G. S., 2012, Ultrasound and deep eutectic solvent (DES): A novel blend of techniques for rapid and energy efficient synthesis of oxazoles, *Ultrasonics Sonochemistry.*, 20, 287–293.
- Smith EL., Abbott A. P., Ryder K. S., 2014, Deep Eutectic Solvents (DESs) and Their Applications, *Chemical Reviews*, 114, 21, 11060-11082, 2014, DOI: 10.1021/cr300162p.
- Tereshatov E. E., Boltoeva M. Y., Folden C. M., 2016, First evidence of metal transfer into hydrophobic deep eutectic and low-transition- temperature mixtures: indium extraction from hydrochloric and oxalic acids. *Green Chem.*, 18, 4616–4622.
- Teterin V. V., Rymkevich D. A., Kiryanov S. V., Cherezova L. A., 2019, Method for processing of dust wastes formed during cleaning of gases of ore-thermal furnace, C22B7/02, RU 2694862 C1 Patent Office: Moscow, Russian Federation.
- Zhang Y., Li L., Li J., Hua Y., Xu C., Ke P., 2016, Dissolution behavior of zinc oxide in choline chloride-oxalate hydrates deep eutectic solvents. *Zhongnan Daxue Xuebao (Ziran Kexue Ban) / Journal of Central South University (Science and Technology)*, 47, 2591– 2599.