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SEPARATION AND IMMOBILIZATION OF VANADIUM FROM INDUSTRIAL FLY ASH AS AN INSOLUBLE INORGANIC PIGMENT

It has been shown that the precipitation of bismuth orthovanadate from a fly ash leachate is a promising method of vanadium recovery. $BiVO_4$ obtained after appropriate heat treatment can be sold as a pigment. The yield of recovery of solubilised vanadium is equal to 68% and the precipitate is free from nickel impurity. The precipitate is insoluble in the solutions with $pH \geq 3$. In more acidic media the solubility of precipitate increases with the decreasing pH. The solubility of the precipitate increases also with the increasing concentration of chloride ions.

Keywords: recovery, inorganic pigments, solubility, vanadium, bismuth, immobilisation

1. Introduction

Although global investments in renewable energy are constantly growing, the combustion of fossil fuels is still the main source of electricity. Coal and natural gas are the most important fossil fuels on a global scale (Fig. 1). However, there are some countries, such as Eritrea, South Sudan, and Malta, where electricity production is almost exclusively based on the combustion of heavy oil. It is also the major source of energy (ca. 60% of production) for Kuwait, and Yemen. Even bigger countries like Ecuador, Egypt, Venezuela and Argentina use a significant amount of oil to produce electricity. Combustion of heavy oil in 2016 gave 931 TWh of electricity which accounts for 3.3% of the world's production [1].

Similarly to other fossil fuels, the combustion of heavy oil has a negative environmental impact. Besides CO_2 emission, burning of 1 m^3 of oil gives about 2.5 kg of the fly ash. It contains heavy metals such as vanadium and nickel, both in the form of oxide phases [2,3].

Chemical composition of the fly ash varies in a wide range and depends on the chemical composition of the oil and combustion conditions (Table 1). Values reported in literature depend also on analytical procedures applied and can be difficult to compare. For instance, Xiao et al. dried the fly ash at 105°C for 48 h, the content of moisture was determined as 10 wt.%, mineralised
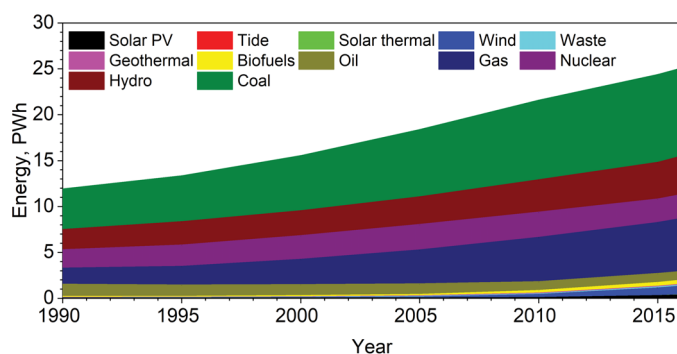

Fig. 1. World power generation by fuels between 1990 and 2016 [1]

and analyzed the chemical composition of the solution using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). Carbon and sulphur content was determined using LECO analysis method [4,5]. The same procedure was adopted by Seggiani, however, their specimen was not dried [13]. Other authors reported only the content of metals in the ash, based on Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) [16] and Atomic Absorption Spectroscopy AAS [17]. Navarro, in turn, heated the ash at 110°C to constant weight, mineralised and analysed the chemical composition of the solution using ICP-AES. Carbon content was only estimated as the weight loss of the specimen after annealing at 1000°C for 6 h

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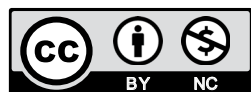
Chemical composition of the fly ash in wt.%, reported in the literature

V	Al	Ca	Fe	Mo	Ni	Si	Ti	C	S	Mg	Na	K	Zn	Cr	Co	P	Mn	Pb	Cu	LOI	Literature
3.58	12.70	0.80	5.63	0.23	1.12	26.20	1.65	—	—	—	—	—	—	—	—	—	—	—	—	27.3	[6]*
2.10	8.19	0.82	8.93	0.24	0.66	21.00	2.24	—	—	—	—	—	—	—	—	—	—	—	—	89.5	[7,8]*
1.78	5.87	2.00	3.49	0.13	0.57	36.00	1.17	—	—	—	—	—	—	—	—	—	—	—	—	50.6	
2.08	7.43	1.05	14.90	0.20	0.59	20.80	1.75	—	—	—	—	—	—	—	—	—	—	—	—	91.0	
3.02	12.20	1.11	5.33	0.17	1.00	22.80	2.02	—	—	—	—	—	—	—	—	—	—	—	—	58.6	[8,9]*
3.02	11.20	1.77	4.41	0.17	0.95	25.00	1.72	—	—	—	—	—	—	—	—	—	—	—	—	62.0	
2.49	13.00	0.86	3.66	0.11	0.82	23.00	1.84	—	—	—	—	—	—	—	—	—	—	—	—	35.4	
3.63	12.10	0.77	3.83	0.28	1.05	27.20	1.89	—	—	—	—	—	—	—	—	—	—	—	—	88.4	
3.58	12.70	0.80	5.63	0.23	1.12	26.20	1.65	—	—	—	—	—	—	—	—	—	—	—	—	27.3	
3.19	13.10	1.18	5.65	0.18	1.01	26.40	1.46	—	—	—	—	—	—	—	—	—	—	—	—	26.7	
3.02	11.00	1.27	5.49	0.19	0.97	25.20	1.62	—	—	—	—	—	—	—	—	—	—	—	—	58.9	
2.86	10.70	1.67	5.11	0.2	0.92	28.40	1.43	—	—	—	—	—	—	—	—	—	—	—	—	23.1	
3.0	12.20	1.20	5.20	0.20	1.00	25.70	1.70	—	—	—	—	—	—	—	—	—	—	—	—	35.0	[10]*
9.6	1.20	3.00	0.50	—	3.00	—	—	7.10	13.20	9.10	1.10	0.60	—	—	—	—	—	—	—	—	[11]
1.60	0.64	0.20	1.70	—	0.85	3-4	—	—	—	0.14	—	—	—	—	—	—	—	—	—	85.0	[12]*
0.77	0.29	—	5.98	—	1.80	—	—	—	—	0.34	—	—	0.11	—	—	—	—	—	—	—	[13]
5.00	—	—	22.10	0.35	1.54	—	—	—	—	0.20	—	—	—	0.80	0.22	—	—	—	—	—	[14]
27.60	0.06	0.79	0.77	—	5.93	0.27	0.13	36.5	12.80	2.66	1.39	0.08	0.05	0	—	0.02	0.02	0.06	0.05	—	[4,15]*

LOI – loss on ignition

* – indicates that the ash was annealed or dried prior analysis of chemical composition.

[14]. Etsell et al. heated their specimens to constant weight at 500°C, mineralized and determined metals and silicon content in the solution using AAS [8-12].

Major component of the ash is unburned fuel (i.e. mainly carbon). Therefore, LOI (loss on ignition) values are high and sometimes achieve 90%. The fly ash can also contain significant amount of Si in the form of SiO_2 (quartz and cristobalite) and aluminosilicates such as mullite $3Al_2O_3 \cdot 2SiO_2$ [4,8,11] as well as S in the form of sulphates [4]. Since vast majority of crude oils contain metals: Na, K, Li, Ca, Sr, Fe, Cu, Ag, Mn, Sn, Pb, Co, Ti, Au, Cr, V and Ni (see Table 1), they are also found in the fly ash. The most important, from the practical point of view, are vanadium and nickel. The former occurs mainly in the form of water soluble vanadyl sulphate $VOSO_4 \cdot 3H_2O$ whereas nickel as nickel dithionate $NiS_2O_6 \cdot 6H_2O$ [4,5] and nickel titanate $NiTiO_3$ [9,10]. Vanadium content in the fly ash varies in a very wide range between 0.77 and 27.6 wt.%, however the most common value is around 2 wt.%. It is over two times higher when compared to vanadium content in the ore from Bushveld deposit in South Africa. Total amount of V in the ash exceeds current world consumption of this metal [5]. Nickel content is similar, usually around 1 wt.% (Table 1).

Fly ash can also contain significant amount of iron, in the form of hematite Fe_2O_3 and pseudobrookite $FeTiO_5$ [9,10], and, usually less calcium and magnesium, as sulphates: $CaSO_4$ [9,10] and $MgSO_4 \cdot 6H_2O$ [4,5]. It should be noted here that precise determination of phase composition of the fly ash is difficult due to its poor crystallinity and huge amount of possible phases.

A number of recovery processes of vanadium from the fly ash have been reported: alkali melting and roasting, oxidising roasting, chloridising roasting and leaching [16]. The latter seems to be the most interesting, due to high solubility of the fly ash in aqueous solutions. However, efficient methods of recovery of vanadium and nickel from the leachate must be proposed.

The fly ash readily dissolves in alkaline solution. When the leaching process was carried out in 2 M sodium hydroxide solution, 80% of vanadium from the ash was dissolved. However, the extraction of nickel was only negligible. Utilisation of 4 M NH_3 increased the yield of nickel extraction up to 60% [17]. Akita et al. [18] proposed a two-step process. At first, nickel oxide is selectively leached using NH_4Cl solution with yield ca. 59.1%, whereas only 0.6% of vanadium is dissolved. Then, remaining vanadium oxide is leached with Na_2CO_3. The major advantage of the alkaline process is that iron is not leached from the ash.

Leaching process can also be performed in acidic media. When it is carried out in 0.25 M sulphuric(VI) acid, 65% vanadium and 60% of nickel is dissolved. The leaching yield increases with the increasing concentration of H_2SO_4 [19]. The nitric(V) acid was also successfully applied for nickel dissolution. When its concentration was equal to 30%, almost 80% of nickel was dissolved at 60°C. Again, the increase of acid concentration is beneficial for the leaching yield [20].

Recovery of vanadium and nickel from the leachate is usually performed using ion exchange resins, solvent extraction and adsorption. Process using ion exchange seems to be the most effective. Two types of ion exchange resins, strongly acidic (DIAION SK1B) and chelatic (DIAION CR11, DIAION CR20, DUOLITE C467) were investigated. It was shown that more than 80% of V and Ni can be recovered from the leachate on C467 and CR20 resins. C467 possesses the highest selectivity for vanadium extraction against iron [13]. The ion exchange

resins Amberjet 4200 Cl and Amberjet 1200 H where also successfully applied for V and Ni recovery [21].

Akita et al. [18] used solvent extraction for vanadium recovery from leachate. Two extraction solvents were tested: tri-n-octylamine (TOA) and tri-n-octylmethylammonium chloride (TOMAC). The latter exhibited lower extraction rate, as well as lower efficiency during the stripping process [18].

Adsorption on activated carbon was successfully applied for recovery of 95% of Ni from the leachate containing aqueous ammonia. However, vanadium recovery yield was only 35% [21].

Therefore, there is still room for improvement in the field of V and Ni recovery from leachate. Precipitation of vanadium as bismuth orthovanadate may be interesting alternative for ion exchange, solvent extraction and adsorption. $BiVO_4$ exists as one of the 4 known polymorphs: tetragonal-scheelit type and monoclinic-scheelit type (clinobisvanite), tetragonal-zircon type (dreyerite) and orthorhombic (pucherite) [22-25]. Scheelit-type phases are the most important.

From the scientific point of view, clinobisvanite attracts significant attention due to its promising photocatalytic properties [25-32]. From the industrial point of view, in turn, both monoclinic and tetragonal scheelite-type phases are important. They exhibit brilliant yellow colour and almost the same value of the band gap (2.4 and 2.3 eV respectively). Thus, they are industrially applied as pigment (C.I. Pigment Yellow 184) [33-35]. Two methods of synthesis of $BiVO_4$ are used in the pigment industry. The first one is solid state reaction between Bi_2O_3 and V_2O_5 at elevated temperature (500°C). The other one, more suitable, is precipitation from an aqueous solution. At first, metallic bismuth is dissolved in HNO_3 and $Bi(NO_3)_3$ solution is obtained; then sodium metavanadate is added. Precipitation occurs, when the pH of the solutions is raised with NaOH. The precipitate, which consists of oxides and hydroxides, is then washed with water and heated to reflux to obtain desired scheelit-type phase [35].

In this work, bismuth orthovanadate was precipitated from the acidic fly ash leachate, using bismuth nitrate, similarly to the process adopted in the pigment industry. Thus, the possibility of vanadium recovery has been demonstrated. Due to the lack of literature data concerning solubility of $BiVO_4$ in acidic solutions, the influence of concentration of H_2SO_4 on the solubility of obtained $BiVO_4$ has also been investigated. If the chloride ions, are present in the leachate, they can complex bismuth ions, which leads to decrease of the recovery yield. Therefore, the influence of Cl^- concentration in acidic solution on the solubility of bismuth orthovanadate has also been studied.

2. Experimental

The fly ash was obtained from our industrial partner. Its chemical composition was determined using X-ray photoelectron spectrometer (XPS, Gammadata Scienta SES R4000) equipped with a hemispherical analyser. The Mg Kα source of incident energy of 1256.6 eV was applied to generating core excitation. The power of the source was equal to 180 W. The spectrometer was calibrated according to ISO 15472:2001. The energy resolution of the system, measured at full width at half maximum (FWHM), for Ag 3d5/2 excitation line, was 0.9 eV.

In this work, 15 g of the fly ash was leached using 1 dm^3 of 0.02 M sulphuric(VI) acid at the room temperature. Leaching time was 60 minutes, the reaction mixture was vigorously stirred (800 rpm). However, it was not dissolved completely. Then, the solution was filtered to separate the leachate from the residues. The solution obtained in such a way was applied for all experiments related to the vanadium recovery.

Quantitative analysis of the chemical composition of the ash was performed in the following way. First, the specimen (0.6423 g) was annealed in air at 550°C for 24 h to remove carbon, possibly sulfur and water. The remaining (0.3519 g) was then dissolved in 100 cm^3 of hot (80°C) aqua regia vigorously stirred (800 rpm) for 4 hours. Obtained solution was clear. This solution was analysed using Microwave Plasma Atomic Emission Spectroscopy (MP-AES). Sulfur and carbon content was determined independently to their oxidation state and chemical structure using LECO CS600.

The chemical composition of the former was obtained using the microwave plasma – atomic emission spectrometer Agilent MP-AES 4200, which was equipped with a standard torch, OneNeb nebulizer, double pass glass cyclonic spray chamber, Zefiro MP nitrogen generator and autosampler. Standard solutions for MP-AES analysis were obtained from SPEX CertiPrex.

$BiVO_4$ was precipitated from the leachate using bismuth nitrate saturated solution at $T = 50$°C. Bi/V atomic ratio in the reaction mixture was equal to 1, 1.1, 1.2 and 1.3. $Bi(NO_3)_3$ solution was acidified with HNO_3 (5 cm^3 of 65% HNO_3 in ca. 25 cm^3 of water) in order to avoid its hydrolysis. Then, the pH of the reaction mixture was increased to 2.1 using aqueous ammonia (25% v/v). After 10 minutes of continuous stirring, precipitate was filtered out. Its phase composition was obtained using X-ray diffractometer Rigaku Miniflex II, chemical composition, in turn, using XRF and XPS spectrometers.

The solubility of bismuth orthovanadate, precipitated from the leachate, was studied at 19 ± 1°C, in H_2SO_4 aqueous solutions, as the function of their pH, within the range 1-5. The influence of Cl^- content (between 0.18 and 8.86 $g \cdot dm^{-3}$) in sulphuric acid was also determined, at pH = 2. Additionally, $BiVO_4$ solubility in 0.1 M HCl and in the mixture of 0.1 M HCl and 0.9 M $HClO_4$ was established. The following procedure was adopted: around 0.1 g of the salt was suspended in 100 cm^3 of aqueous solution and stirred for 14 days using magnetic stirrer (800 rpm rotation speed). The chemical composition of the solutions was then determined using MP-AES. The kinetics of dissolution was also determined, using conductometer / pH-meter CPC-505 (Elmetron, Poland).

The chemical reagents applied (pure grade) were obtained from POCH and Chempur, Poland. All the solutions were made by using deionised water (> 18 MΩ).

The composition of the fly ash was analized using X-ray fluorescence spectrometer (Rigaku Primini II, WD-XRF) and LECO CS.

3. Results and discussion

3.1. Chemical composition of the fly ash and the leachate

Preliminary, qualitative analysis of the chemical composition of the fly ash was performed using XRF and XPS methods. The former indicated presence of the following elements: V, S, Ni, Fe, Na, Si, Al, Ca, Zn, K, P, Cu and Mo. Since the ash contains significant amounts of carbon and sulphur, XRF cannot be used for quantitative determination of the chemical composition of the ash. The latter method confirmed that analysed material contains carbon, oxygen, vanadium, nickel, iron and silicon (Fig. 2). The difference between results obtained using XRF and XPS stems from the average depth of analysis. It is ca. 5-10 nm for the latter and ca. 1000-fold higher for the former. This indicates inhomogeneity of the fly ash. The grains are enriched with sulphur and silicon on the surface whereas metals such as Na, Al, Ca, Zn and K are located in their interior.
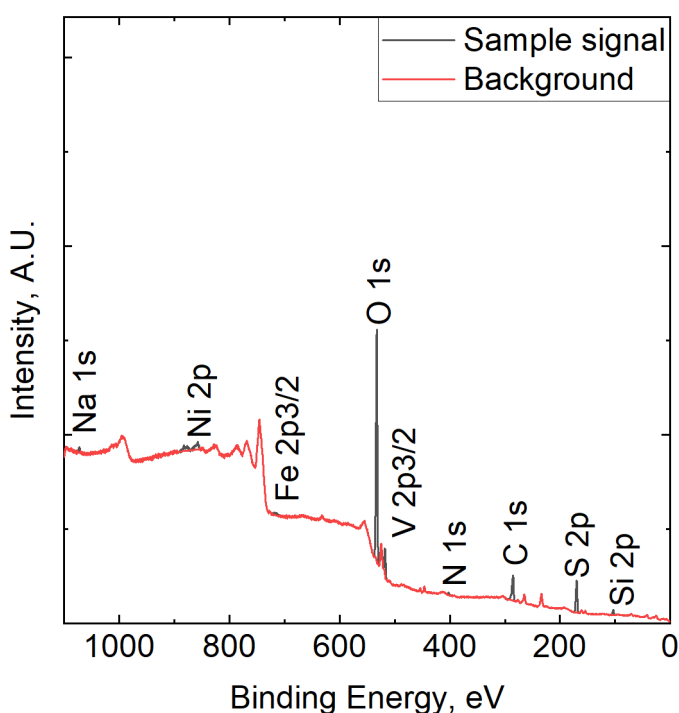
Fig. 2. XPS survey spectra of the fly ash

The chemical composition of the fly ash in the as received state, i.e. without annealing, was determined using MP-AES and LECO (Table 2).

TABLE 2

Chemical composition of the fly ash in the as received state

Concentration, wt.%												
V	Ni	Fe	Cs	Al	Ca	Ba	Mo	Mg	Zn	Ta	C	S
10.59	2.93	2.36	0.28	0.21	0.20	0.13	0.12	0.06	0.06	0.05	5.82	15.00

Vanadium and nickel content in the ash is relatively high when compared to the values from Table 1. Iron and molybde-

num concentration, in turn, is relatively low. The ash contains also small amounts of Cu, Cr and Co (0.02 wt.% each). Silicon content in the ash was not determined.

Since the fly ash is water-soluble, recovery of heavy metals can be done on the hydrometallurgical way. It was easily leached in diluted H_2SO_4 at the room temperature. Chemical composition of the leachate was determined using MP-AES and is given in Table 3.

TABLE 3

Chemical composition of the leachate

Concentration, g·dm^{-3}								
V	Ni	Na	Fe	Ca	Al	Zn	Cu	K
16.98	4.44	4.13	4.10	0.49	0.12	0.06	0.02	*

* – below the detection limits.

It should be noted here that vanadium, nickel and iron content in the ash is slightly lower than in the leachate. However, the uncertainties of concentration values given in Table 3 can be significant since high amount of the ash and high volume of sulphuric acid were used for leaching. Thus, leaching efficiency of these elements is close to 100%.

3.2. BiVO$_4$ precipitation from the leachate

Vanadium and nickel are the primary targets of the recovery process. Unfortunately, significant amount of iron in the leachate may lead to contamination of the precipitate. Therefore, appropriate value of the pH of reaction mixture should be found.

In strongly alkaline solutions, pH > 13, vanadium exists in the form of VO_4^{3-} oxyanions. Upon acidification, numerous species such as $V_4O_{12}^{4-}$, $V_5O_{15}^{5-}$, $H_2VO_4^-$, H_3VO_4, $HV_{10}O_{28}^{5-}$, $H_2V_{10}O_{28}^{4-}$, V_2O_5 and VO_2^+ are formed [36]. Their stoichiometry depends both on the pH of the solution and the total concentration of vanadium. Since the latter was equal to 16.98 g·dm^{-3}, vanadium should be present in the leachate as: $H_2V_{10}O_{28}^{4-}$ in the pH range 3.8-1.75, V_2O_5 in the narrow pH range 1.75-0.75 and VO_2^+ in more acidic solutions. However, the given pH values should only be regarded as approximate. They are affected by changes in the ionic strength, counterion in the solutions and temperature [37]. Blue colouration of the leachate suggests that vanadium is present in the cationic form i.e. VO_2^+. It is stable only when redox potential is above 0 V [38,39]. This situation is likely to occur since leachate contains Fe^{3+} as an oxidising agent.

Leachate contains also significant amount of nickel, which is present in the solution in cationic form. $Ni(OH)_2$ precipitates at pH > 7. Thus, contamination of the precipitate with nickel hydroxide can be avoided in acidic solutions (Fig. 3).

In the case of Fe, there is a high risk of its precipitation in the form of hydroxide, even in the acidic solutions. Therefore, the pH of the reaction mixture should be < 2 (Fig. 3).

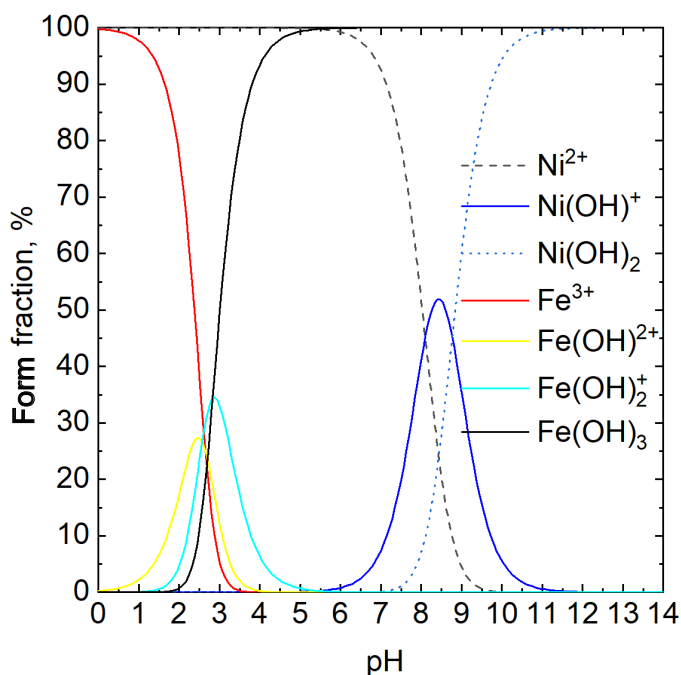Precipitation of $BiVO_4$ can be described according to Eq. (1):

$$Bi^{3+} + VO_4^{3-} \xleftrightarrow{K} BiVO_4 \qquad (1)$$

Fig. 3. Equilibrium predominance diagram for Fe(III)-Ni(II)-OH⁻ system; the calculations were performed for total concentration of iron and nickel equal to 0.08 M, stability constants were taken from the literature [40,41]

Fig. 4. XPS survey spectra of raw $BiVO_4$ obtained when the stoichiometric amount of bismuth salt was added

This equation is applicable for pigment industry, where the reaction mixture can be alkalised to the desired pH value. In this work it was assumed that $BiVO_4$ precipitation is more likely when vanadium is in anionic form, e.g. $H_2V_{10}O_{28}^{4-}$ than cationic. Therefore, the pH of the reaction mixture, after addition of bismuth nitrate, was set at the level of 2.1 using aqueous ammonia. At this pH, small amount of $Fe(OH)_3$ can be precipitated.

Yellow precipitate appeared in the solution when the pH was set to 2.1. Further in this work it will be called "raw $BiVO_4$". The precipitation was assumed to be finished after 1 h of continuous stirring, then the reaction mixture was filtrated. The precipitate was further analysed using XPS method. The survey spectra with chemical composition of raw $BiVO_4$ are shown in Fig. 4.

Raw $BiVO_4$, obtained upon stoichiometric addition of bismuth salt, consists mainly of Bi, V, and O. The presence of C is related to the surface pollution by organic molecules. This was confirmed by high resolution analysis. Vast majority of carbon is in the form of C-C aliphatic structures (63.5%); 17.5 % forms O-C-M structure, where M stands for metal. It suggests admixture of carbonates in raw $BiVO_4$. It is possible, since the solution before precipitation was not degassed by any inert gas. C-OH, C-O-C and C=O bonds were also found (5.5%) in the specimen.

High resolution spectra confirmed that 100% of vanadium ions is directly connected to oxygen (Fig. 5). Interestingly, 20% of vanadium exists as V^{3+} and 80% as V^{5+}. Trivalent vanadium in the raw $BiVO_4$ may be present as vanadium sulphate $V_2(SO_4)_3$. It is a pale yellow salt which slowly dissolves in water [42].

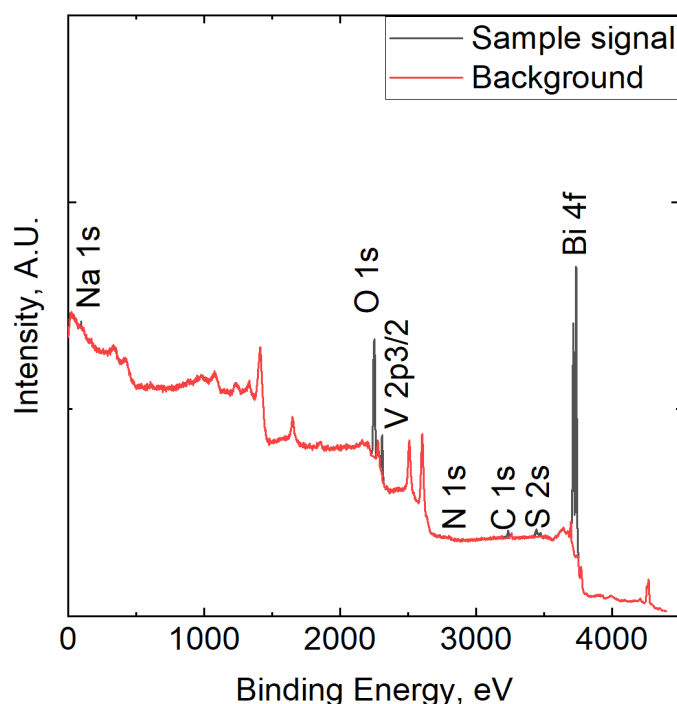It was also found that 100% of bismuth is bounded to oxygen, forming ionic structures. However, the Bi/V atomic ratio exceeds the stoichiometric one significantly. At the same time, raw $BiVO_4$ contains significant amount of sulphur. Therefore, it was assumed that bismuth sulphate $Bi_2(SO_4)_3$ is a component of raw $BiVO_4$ This salt is only moderately soluble in aqueous solutions, even acidic ones [43].

XRD analysis was performed for the raw $BiVO_4$ obtained at the stoichiometric amount of bismuth ions. The results obtained indicate the precipitate is multi-phased and poorly crystalline. Thus, its phase composition was not determined (Fig. 6). Since the colour of the raw $BiVO_4$ obtained is pale yellow, it is also not interesting for the pigment industry.

In the pigment industry, initial $BiVO_4$ precipitate is also amorphous, contains oxides and hydroxides. It is then transformed to finely crystalline, scheelite-type structure, via hydrothermal treatment of the reaction mixture or annealing of the precipitate [28,36]. In this work, raw $BiVO_4$ was also annealed in air at 500°C for 4 hours and desired scheelite-type $BiVO_4$ polymorph was obtained (space group $I4_1/a$, ICDD card 04-010-5710). Vast majority of the diffraction lines were ascribed to this phase (Fig. 6). However, there are still some diffraction lines that originate from the unidentified impurities. In the pigment industry, the quality of the product, e.g. its shade and brilliance depend on the precipitation conditions (concentration of vanadium and bismuth in the solutions, its pH and temperature) [35]. Although the results obtained are promising, the influence of the aforementioned parameters on the precipitation of $BiVO_4$ from the fly ash leachate should be further studied in order to obtain high purity product.

Possibility of vanadium recovery from leachate as scheelite-type $BiVO_4$ was demonstrated. However, another important issue
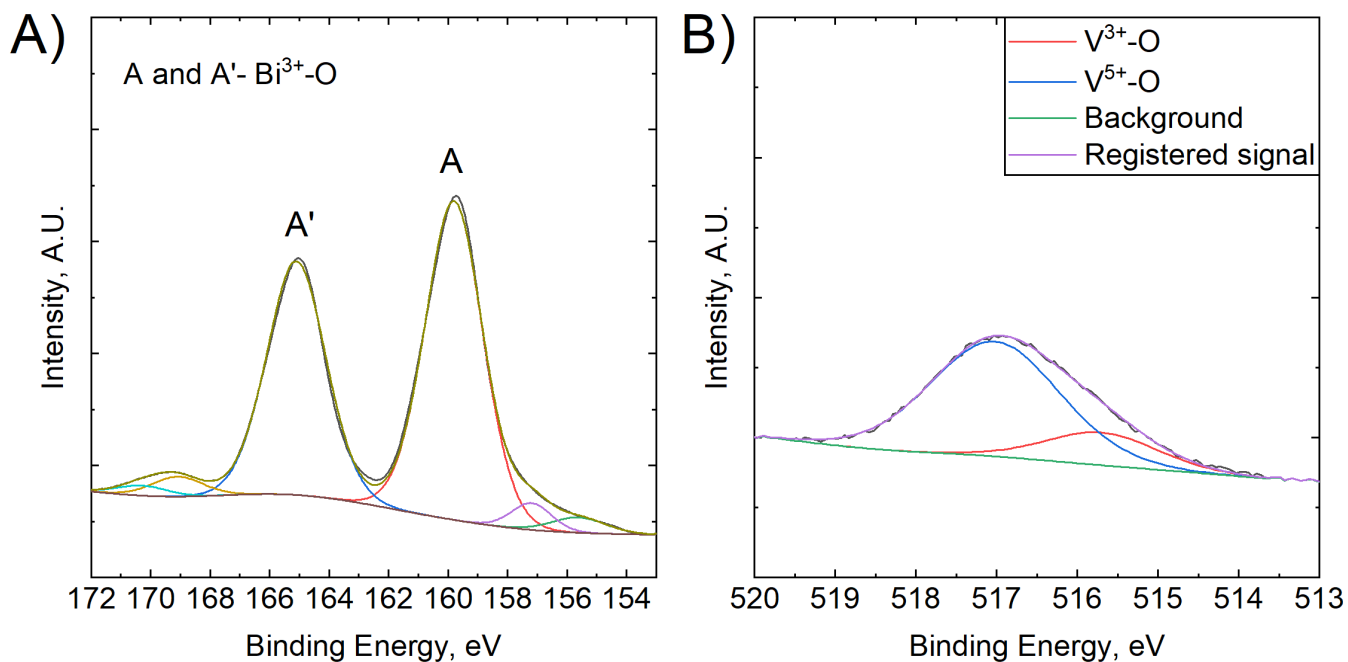
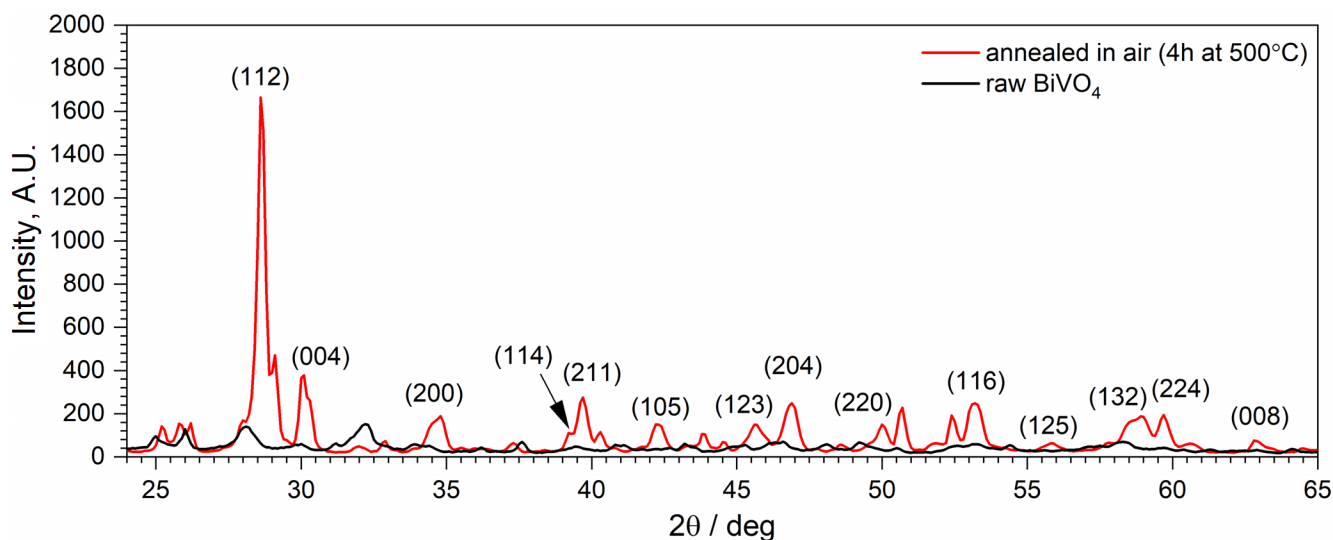Fig. 5. High resolution XPS spectra of bismuth A) and vanadium B)

Fig. 6. Diffraction pattern of raw and annealed $BiVO_4$ obtained when the stoichiometric amount of $Bi(NO_3)_3$ was added to the solution

is determination of the chemical composition of the filtrate. In this work, the content of vanadium, nickel and iron in the filtrate was obtained, using MP-AES method, as the function of Bi/V atomic ratio in the reaction mixture and compared to the chemical composition of leachate (Fig. 7).

It is possible to see that the vanadium concentration in the filtrate decreases as the amount of bismuth nitrate in the reaction mixture increases; the same can be observed for iron. Thus, the reaction product must be contaminated with Fe. The following processes may be responsible for that. The first one is precipitation of small amount of $Fe(OH)_3$ according to Fig. 3. The second one is precipitation of $Fe_4(VO_4)_4$, however, this process is rather slow [44]. The third one is adsorption of iron on the surface of the precipitate. The latter possibility should be excluded since XPS analysis did not indicate presence of iron on the surface

of raw $BiVO_4$. Therefore, iron is precipitated together with raw $BiVO_4$ and probably occluded with this salt in such a way that is not detectable during XPS analysis.

What is also important, nickel concentration in the filtrate does not change. Therefore, selective recovery of vanadium from the leachate is possible. Nickel can be further recovered from the lixiviant using other methods [45,46].

The yield of vanadium recovery increases as the amount of $Bi(NO_3)_3$ in solution increases from 47% for the stoichiometric Bi/V atomic ratio to 68% for 1.3. This clearly indicates that bismuth is consumed in some parasitic reaction which is possibly precipitation of $Bi_2(SO_4)_3$, as it was deduced from analysis of XPS spectra.

The results of the XRF analysis of the precipitate confirm that raw $BiVO_4$ is not the chemically pure compound. It is
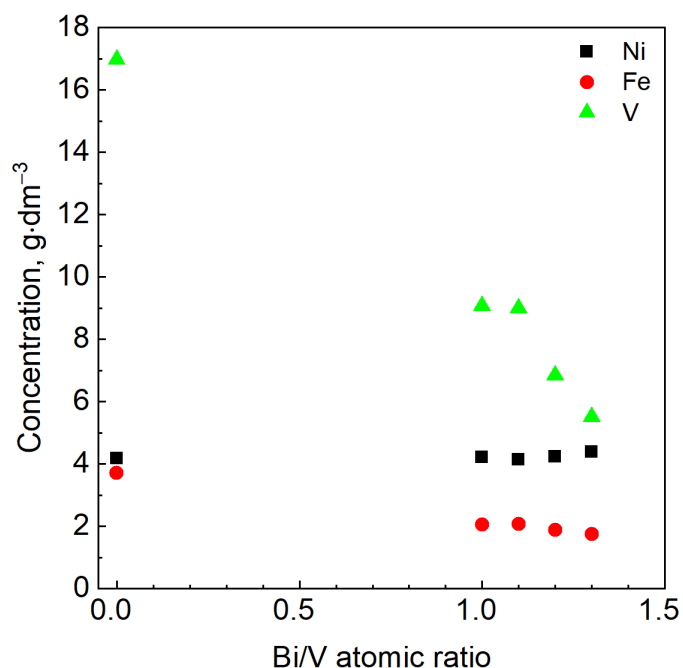
Fig. 7. Chemical composition of the solution after precipitation of raw BiVO$_4$

also contaminated with iron and sulphur. The increase of the concentration of bismuth ions in the reaction mixture slightly increases the vanadium fraction in the raw BiVO$_4$, at the same time, fraction of bismuth and sulphur decreases (Fig. 8).
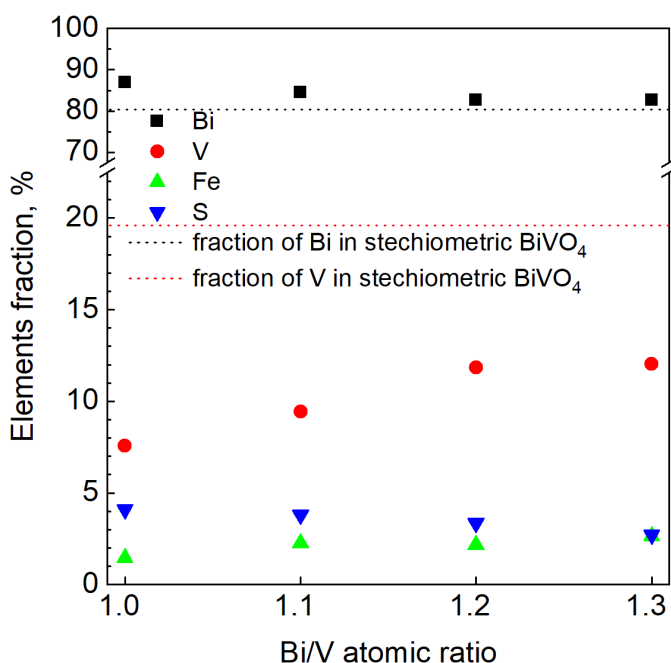

Fig. 8. Chemical composition of raw BiVO$_4$ as the function of Bi/V atomic ratio

3.3. Solubility of raw BiVO$_4$

Solubility of the precipitated salt is important factor influencing the yield of this process. On the one hand, there is no

literature data concerning the solubility of BiVO$_4$. On the other hand, when discussing the process of vanadium recovery, it is more practical to use the solubility of the obtained precipitate, here denoted as raw BiVO$_4$, even if it is not a single-phase one. The results discussed below concern the raw BiVO$_4$ obtained at the stoichiometric amount of bismuth ions added.

The kinetics of dissolution of raw BiVO$_4$ was evaluated using a conductometric method. Conductivity of the solution increases with time due to dissolution of raw BiVO$_4$. It is possible to see, that equilibrium in the system is reached after $t >$ c.a. 80 hours (Fig. 9).

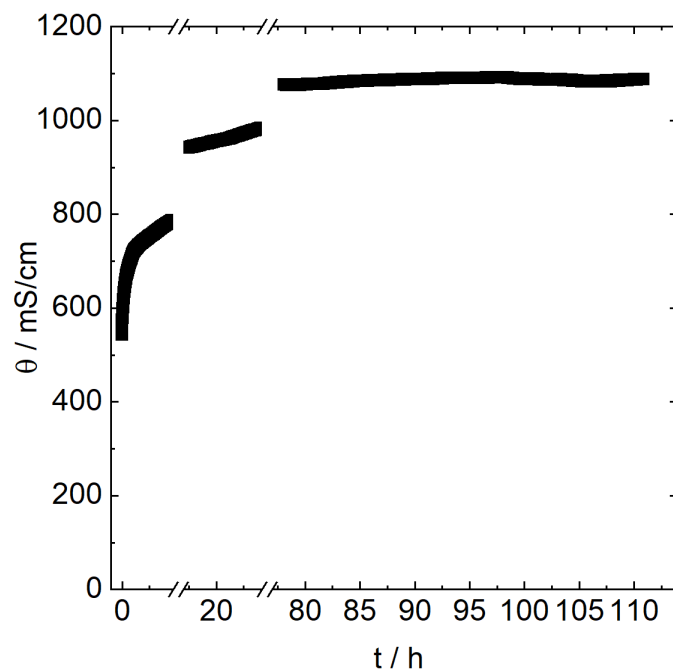Fig. 9. Conductivity of the acidic solution during dissolution of raw BiVO$_4$ (H$_2$SO$_4$, pH = 3, T = 19°C)

Due to the complexity of the system studied, the conductometric method could not be applied for direct determination of the solubility of raw BiVO$_4$. From the practical point of view, the important parameter is the concentration of vanadium in equilibrium with the aqueous phase. It was determined using MP-AES method (Table 4).

TABLE 4

The solubility of raw BiVO$_4$ as a function of pH of H$_2$SO$_4$ aqueous solution, t = 15 days, T = 19°C

pH	Initial mass of raw BiVO$_4$, g	Concentration of V, mg·dm^{-3}
1	0.0998	10 ± 0.03
2	0.1011	0.4 ± 0.01
3	0.1036	0*
4	0.1066	0*
5	0.1000	0*

* – below the detection limits.

It is possible to see that raw BiVO$_4$ is virtually insoluble in aqueous solutions, when pH is ≥ 3. Its solubility in more acidic

solutions is also insignificant. If the precipitation process is performed in the most acidic solution studied (pH = 1), the equilibrium concentration of vanadium in the solution (10 mg·dm^{-3}) equals to 0.06% of the initial content of V in the leachate. It is not important from the point of view of the recovery yield.

It is interesting to compare Fig. 9 and data from Table 4, for pH = 3. On the one hand, the increase of the conductivity is related to dissolution of raw BiVO$_4$. On the other hand, concentration of vanadium in the solution in equilibrium with raw BiVO$_4$ was below the detection limit of the spectrometer. Possibly, bismuth sulphate dissolved during the experiment instead of BiVO$_4$.

It is well known that bismuth(III) ions form stable chloride complexes in aqueous solutions. Therefore, the presence of chloride ions should decrease the vanadium yield in the proposed process. The influence of their concentration on the solubility of raw BiVO$_4$ in H$_2$SO$_4$ solution, at pH = 2, was also investigated (Table 5). It is possible to see that chloride ions indeed increase the equilibrium concentration of vanadium in the solution, thus decrease the yield of V recovery. Although, for the highest Cl$^-$ concentration applied, vanadium concentration increased *ca.* 40 times, its value is still insignificant when compared to the initial concentration in the industrial waste.

TABLE 5

The solubility of raw BiVO$_4$ as the function of Cl$^-$ concentration, H$_2$SO$_4$ aqueous solution, pH = 2, *t* = 15 days, *T* = 19°C

Concentration of Cl$^-$, g·dm^{-3}	Initial mass of raw BiVO$_4$, g	Concentration of V, mg·dm^{-3}
8.86	0.1027	10.01
3.55	0.1000	6.02
1.77	0.1023	3.01
0.35	0.1002	2.20
0.18	0.0997	1.5

The influence of pH at the constant concentration of chloride ions, equal to 3.55 mg·dm^{-3}, was also investigated. As it was expected, the highest concentration of vanadium has been obtained when the pH = 0 (0.1 M HCl, 0.9 M HClO$_4$). It is equal to 56.23 ± 0.34 mg·dm^{-3}. At pH = 1 (0.1 M HCl), the concentration of vanadium in the solution is higher and equals to 62.67 ± 0.24 mg·dm^{-3}. At pH = 2, its concentration is *ca.* 10 times lower (6.02 ± 0.31 mg·dm^{-3}).

4. Conclusions

The possibility of precipitation of scheelite-type BiVO$_4$ from the leachate was demonstrated. Therefore, proposed method of vanadium recovery from the fly ash leachate seems to be the promising one. However, results presented in this work are only preliminary and further investigations are necessary for better understanding the studied system.

First of all, precipitation conditions should be optimised in order to obtain pure, scheelite-type BiVO$_4$ after annealing. This

can be achieved by careful controlling the chemical composition of the reaction mixture and temperature. High purity of BiVO$_4$ is necessary for its application as a pigment.

Vanadium yield should also be increased. It was found that it is not affected with solubility of raw BiVO$_4$. However, significant amount of sulphur in the ash and presence of trivalent vanadium species decrease the recovery yield. In order to decrease the amount of sulphur in the ash, it should be roasted in oxidative environment as a pre-treatment. During oxidative roasting sulphates will thermally decompose and lower amount of bismuth nitrate will be consumed during precipitation of raw BiVO$_4$. Roasting should also decrease the amount of carbon in the ash and thus increase the leachability of the ash.

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