



# Vanadium – Valuable and toxic element in coal combustion ash: An overview

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## ABSTRACT

The paper evaluates all important aspects related to V present in coal and its behaviour during coal combustion with particular attention paid to its potential extraction from ash and slag wastes. Due to great environmental benefits of co-combustion of coal and wastes, these alternative fuels and corresponding ash and slag counterparts were also taken into evaluation. Specifically, the paper summarizes V levels in world coals, in other related materials (alternative fuels, additives etc.) and in ash and slag residues including V speciation and discussion of its valence states. Theoretically predicted (equilibrium-based) calculations and species are compared with experimental results; due to a significant effect on mitigating CO<sub>2</sub> emissions, attention is paid also to oxy-fuel combustion conditions. With the aim to extract V out of the ash and slag residues, physical, chemical, and biotechnological separation methods are discussed in detail along with dominant affecting factors. The paper includes also concluding remarks and highlights the most promising trends and limitations thereby providing suggestions for future research.

## 1. Introduction

Annual production of V is estimated to be around 100.000 t (Bielowicz, 2020; Chinach, 2020); the largest producers are China, South Africa and Russia (Bielowicz, 2020). V is widely used in industrial applications. Due to its high tensile strength, hardness, and fatigue resistance, about 85% of V is used in the production of high-strength ferrous and non-ferrous alloys (Moskalyk and Alfantazi, 2003). According to Moskalyk and Alfantazi (Moskalyk and Alfantazi, 2003) there is still no acceptable substitute for V in the production of aerospace Ti alloys. Other important applications are production of catalysts, inks, dyes, pigments for ceramics and textile industry, batteries, or materials for nuclear reactors (Bielowicz, 2020; Zhang et al., 2019a; Font et al., 2007).

According to European Commission (2020), V belongs to the 2020 list of critical raw materials, i.e., materials that are the most important economically and with a high supply risk – possible interruption in V supply would have harmful consequences on economy (European Commission, 2020). V is the 22-th the most abundant element in earth crust with average concentration of 150 g/t (Fleischer, 1953; Zhang et al., 2019a). As V is not present in high concentrations in minerals, other sources are typically used – it can be recovered as a by-product

during extraction of other components from petroleum residues, metallurgical slags, ore concentrates, waste materials etc. (Moskalyk and Alfantazi, 2003; Vitolo et al., 2000; Bielowicz, 2021).

Combustion residues (ashes or slags) are typical industrial wastes produced in vast quantities throughout the world, e.g. in India (112 Tg/y), China (100 Tg/y), USA (75 Tg/y), Germany (40 Tg/y), UK (15 Tg/y), Poland (4 Tg/y) etc. (Świetlik et al., 2012; Zhao et al., 2018a). Combustion ashes/slags are therefore intensively studied as a possible source of valuable components, such as char (Badenhorst et al., 2020; Bartoňová, 2015; Nunes et al., 2022; Hower et al., 2017), alumina (Guo et al., 2019), Ge-Ga (Dai et al., 2014a; Zhou et al., 2021), REE (Wagner and Matiane, 2018; Fu et al., 2022; Hower et al., 2020, 2016; Valentim et al., 2019) or Y (Bartoňová et al., 2018; Vassilev and Vassileva, 2020). Unfortunately, papers evaluating combustion ashes as an available source of V are very scarce or nearly non-existent.

During coal combustion, V present in input fuel is redistributed among emissions and solid combustion residues – ashes or slags. Due to medium/low V volatility, environmental research is primarily focused to other (usually more volatile) elements. Therefore, papers dealing with mitigating gaseous emissions are focused predominantly to Hg (Wierońska et al., 2018; Scala et al., 2011; Hower et al., 2005), As (Wierońska-Wiśniewska et al., 2022; Fu et al., 2021), Se (Yu et al., 2022), Pb

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(Bartoňová et al., 2019; Zhao et al., 2018b, 2017), Cd (Bartoňová et al., 2020; Fu et al., 2019a), Cu and Zn (Zha et al., 2018, 2020) or Cr (Zhao et al., 2018b; Bartoňová and Raclavská, 2022; Wagner et al., 2021; Fu et al., 2019b).

Hence, due to medium/low V volatility, large proportion of V is bound in combustion ashes/slugs, which may hinder their further technological use, handling, storage, or landfilling. According to EPA report from 2011 (US EPA, 2011), V is included in two pollutant groups – “Heavy metals” and “Inorganic pollutants”. Exposure to V compounds may cause coughing, irritation of upper respiratory tract, gastrointestinal diseases, or conjunctivitis. The toxicity depends on V speciation and generally increases with increasing valence state – pentavalent V species are the most toxic (Barceloux and Barceloux, 1999; Navarro et al., 2007). Therefore, V is traditionally considered as an element of environmental concern (Wagner and Hlatshwayo, 2005; Vassilev et al., 2014; George et al., 2008; Goodarzi, 2002; Swaine, 1990; Duchesne et al., 2018). Out of this perspective, recovery of V from solid combustion wastes can lead to multiple benefits – providing critical metal while enhancing the perspectives of the combustion wastes for their further technological use.

Due to rapid urbanization and population growth, generation of other than industrial wastes is growing fast as well (Tun et al., 2018; Tun and Juchelková, 2019a). The co-combustion of coal and biomass, municipal solid waste etc. contributes to CO<sub>2</sub> neutral conversion and climate change benefits (Xu et al., 2020; Zhou et al., 2014a; Růžicková et al., 2018). It addresses both the depletion of fossil fuels and environmental problems with greenhouse gas emissions; moreover, in case of certain wastes, thermal treatment is taken into consideration if there is a danger of releasing harmful organic pollutants during landfilling or if mechanical recycling is for any reasons problematic (Kucbel et al., 2019; Raclavská et al., 2018). Therefore, it is not surprising that thermochemical conversion of wastes and biomass is one of the most actively studied areas in the world science (Vershinina et al., 2022; Corsaro et al., 2016; Demirbas, 2004). However, different composition and other characteristics of such ash and slag wastes require attention due to their broad variability in dependence of the waste material used

(Růžicková et al., 2018; Vassilev et al., 2015; Demirbas, 2004).

For the aforementioned reasons, this review paper evaluates all important aspects related to V present in coal and its behaviour during coal combustion with particular attention paid to its potential extraction from ash and slag residues. Due to great environmental benefits of co-combustion of coal and wastes, these alternative fuels and corresponding ash and slag counterparts were also taken into evaluation. The scheme of the evaluated research area is depicted in Fig. 1. Specifically, Section 2 summarizes V levels in world coals as well as in other related materials (biomass, additives etc.) and Section 3 deals with thermodynamic equilibrium predictions. Section 4 evaluates concentration of V in ash and slag residues including the effect of operating conditions (e.g., oxy-fuel combustion) and V speciation. Section 5 discussed physical separation methods and their efficiency if applied on ash and slag wastes, while Section 6 provides an overview of chemical and biotechnological ways of V extraction from these materials. Section 7 includes concluding remarks and highlights the most promising trends (as well as the limitations) providing suggestions for the future research.

2. V in coals and other related materials

2.1. V concentrations

Concentrations of V in coal combustion ashes/slugs are given not only by operating conditions but namely by V levels in coal; in case of co-combustion with other materials (wastes) V levels therein also affect the resulting concentration in ash/slag.

Examples of V concentrations in coals from world coal regions are summarized in Table 1; concentrations in coal gangue/rejects and limestone (typically used as desulfurization additive) are listed in Table 2.

World averages for low-rank and high-rank coals are 22 and 28 ppm (g/t) V (Ketris and Yudovich, 2009); nevertheless, the data from Table 1 document broad fluctuation (variability) even within 1 seam or coal-field. There are coals containing a few ppm V as well as coals with a few hundred ppm V. Most world coals contain V content below 100 ppm

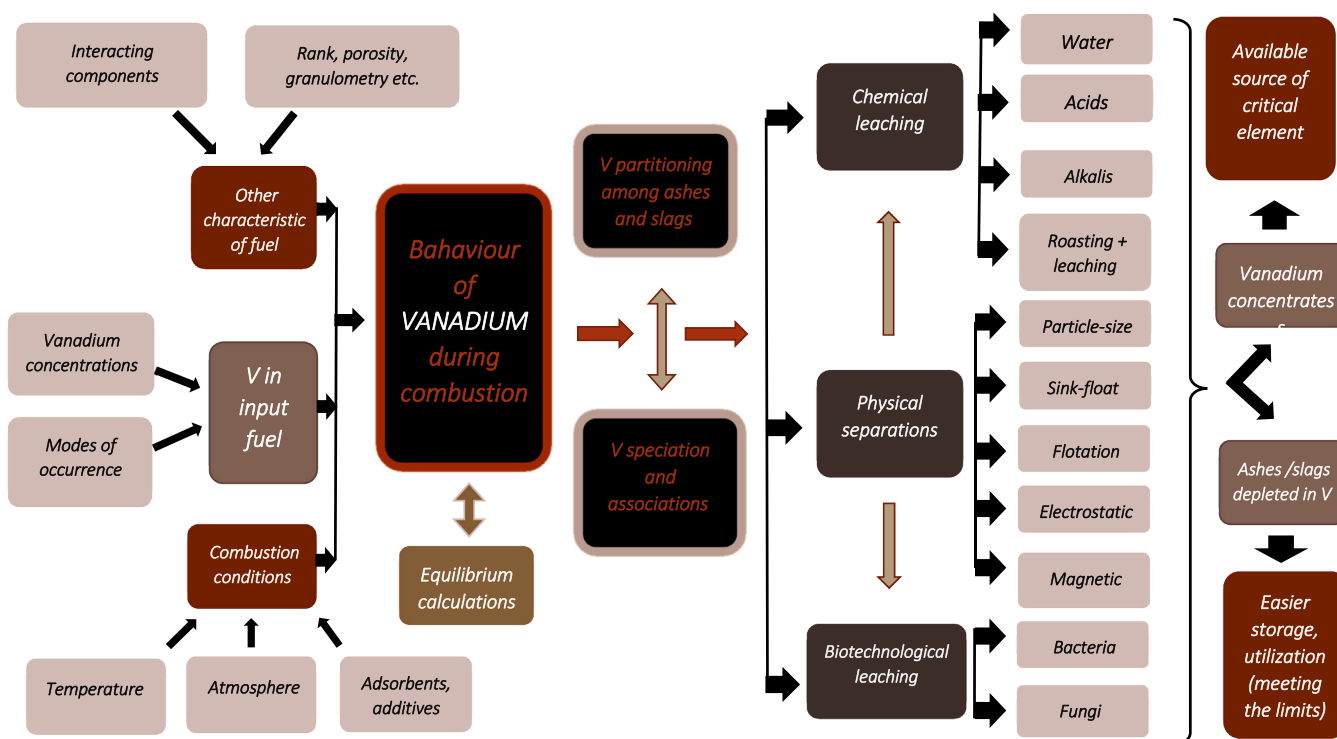


Fig. 1. Classification diagram describing evaluated research area.

**Table 1**  
V concentrations (in ppm or µg/g) in coals from world coal regions.

| Region          | Coal   | Concentrations  | Ref.   |
|-----------------|--|---|--|
| World           | World average lignite (3889 coals)             | Arithmetic mean 37.28<br>Central range 1.2–191.6<br>Maximum 843.0 | (Bouška and Pešek, 1999)                                 |
|                 | World low rank coal                            | 22 ± 2  | (Ketris and Yudovich, 2009)                              |
|                 | World hard coal                                | 28 ± 1  | (Ketris and Yudovich, 2009)                              |
|                 | World total (all coals)                        | 25  | (Ketris and Yudovich, 2009)                              |
|                 | World coals                                    | 2–100 (for most coals)  | (Swaine, 1990, 2000)                                     |
| Northern Europe | 4 Northern European peats                      | 0.51–11.3 (mean 4.2)  | (Klavins et al., 2009; Růžicková et al., 2019a)          |
|                 |  |   |  |
| Australia       | 35 Gunnedah Basin Coals                        | 6.90–1436.0 (mean 153.15)   | (Ward et al., 1999)                                      |
|                 | Australian coals                               | 2–279   | (Swaine and Goodarzi, 1995)                              |
| Brazil          | 7 feed coals                                   | 97.54–124.07  | (Silva et al., 2010)                                     |
|                 | 57 Brazilian coals                             | 23–86   | (Pires and Querol, 2004)                                 |
| Bulgaria        | 4 coals  | 71–87   | (Cutruneo et al., 2014)                                  |
|                 | Santa Catarina coal                            | 104 (mean)  | (Oliveira et al., 2012)                                  |
|                 | Underground mine coals                         | 17 ± 7.9  | (Eskenazy and Stefanova, 2007)                           |
|                 | Open-pit mine coals                            | 19 ± 5.9  | (Eskenazy and Stefanova, 2007)                           |
|                 | Dobrudza deposit Bobov dol                     | 42 ± 20<br>76   | (Eskenazy, 2009)   |
| Canada          | 5 raw coals                                    | 51–116  | (Yossifova, 2014)  |
|                 | White Wood Mine coal Alberta                   | 4.79–56.83  | (Gentzis and Goodarzi, 1999)                             |
|                 | Genesee Mine coal                              | 2–83  | (Pollock et al., 2000)                                   |
| Colombia        | 6 feed coals                                   | 8.70–18.0   | (Goodarzi, 2002)   |
|                 | Canadian coals                                 | 23–300  | (Swaine and Goodarzi, 1995)                              |
|                 | 7 commercial feed coals (exported to Portugal) | < 8–32 (mean 18)  | (Santos et al., 2022)                                    |
| China           | 1324 Chinese coals                             | 35.1  | (Dai et al., 2012)                                       |
|                 | 1123 Chinese coals                             | 51.18   | a (Bai et al., 2007)                                     |
|                 | 1266 Chinese coals                             | 35.05   | a (Ren et al., 2006)                                     |
|                 | 1257 Chinese coals                             | 25  | a (Tang and Huang, 2004)                                 |
|                 | 28 coals from 28 Chinese provinces             | 46.81 (arithmetic mean)<br>35.81 (weighted average)               | (Liu et al., 2017)                                       |
|                 | Lvshuidong mine drillhole                      | 16.9–195, weighted average 68.4                                   | (Dai et al., 2014b)                                      |
|                 | 10 Leping coals                                | 22–105  | (Querol et al., 2001)                                    |
|                 | Jungar basin coals                             | 10–200, average 27  | (Dai et al., 2008)                                       |
|                 | Yudai coal mine                                | 32–201  | (Li et al., 2020)  |
|                 | Jinqi coal mine                                | 31–398  | (Li et al., 2020)  |
| India           | Haerjiao coal                                  | < dl - 33   | (Li et al., 2019)  |
|                 | Meghalaya coalfield                            | 25–500 (in coal ash)  | (Mukherjee et al., 1992)                                 |
|                 | Upper Assam coalfield                          | 200–600 (in coal ash)   | Mukherjee et al. (1992)                                  |
|                 | Jammu coalfield                                | 30–150 (in coal ash)  | Mukherjee et al. (1992)                                  |
| Iran            | 4 Alborz coals                                 | 11–16   | (Goodarzi et al., 2006)                                  |
|                 | South Africa                                   | 23–37   | (Wagner and Hlatshwayo, 2005; Wagner and Tlotleng, 2012) |
|                 | Witbank coalfield (no. 4 seam)                 | 39.2  |  |

**Table 1 (continued)**

| Region | Coal                           | Concentrations               | Ref.   |
|--------|--------------------------------|------------------------------|--|
|        |                                |                              | (Bergh et al., 2011; Wagner and Tlotleng, 2012)      |
|        | Witbank coalfield (no. 2 seam) | 27                           | (Cairncross et al., 1990; Wagner and Tlotleng, 2012) |
|        | Waterberg coalfield            | 85–150                       | (Faure et al., 1996; Wagner and Tlotleng, 2012)      |
| Spain  | Spanish subbituminous coal     | 58.2                         | (Querol et al., 1995)                                |
|        | 4 Puertollano coals            | 66–265                       | (Font et al., 2010)                                  |
|        | Puertollano coals (2 mines)    | 13–89                        | (Alastuey et al., 2001)                              |
| Turkey | 143 Turkish coals              | 5.5–270 (mean 65, median 52) | (Palmer et al., 2004)                                |
|        | 13 Turkish coals               | 65–219                       | (Karayigit et al., 2000)                             |
| UK     | Soma coals                     | 97 and 163                   | (Karayigit et al., 2007)                             |
|        | 24 UK coals                    | 6.6–93 (average 31.6)        | (Spears and Zheng, 1999)                             |
| USA    | Parkgate coal                  | 25.1 (median)                | (Spears, 2015, 2017)                                 |
|        | 142 Gulf Coast coals           | 4.9–110 (median 28)          | (Palmer et al., 2004)                                |
|        | 205 Fort Union coals           | 1.1–110 (median 7.4)         |  |
|        | Average in U.S. coals          | 22                           | (Orem and Finkelman, 2003)                           |
|        | U.S. coals                     | 0.14–370                     | (Swaine and Goodarzi, 1995)                          |
|        | 3 Appalachian coals            | 4.61, 3.63 and 20.54         | (Hower et al., 2015)                                 |

<sup>a</sup> Papers in Chinese reviewed by Dai et al (Dai et al., 2012).

(Swaine, 2000); V concentrations in coal gangue, wastes, rejects or inclusions are generally moderately higher whereas V levels in limestone are lower compared to coals (Table 2). Absolutely the highest V concentration relates to petcoke; therefore, if such material is added to coal during combustion (gasification), the ashes/slugs produced contain substantially higher V concentrations (which is undesirable from environmental point of view but advantageous in terms of searching for available V source).

## 2.2. Modes of occurrence of V

Not only total concentration but also modes of occurrence of V in coal affect its levels in the combustion residues. According to Finkelman et al. (2018), in high-rank coals 65% of V is associated with (alumino) silicates (probably clays) and 35% is organically associated, whereas in low-rank coal the proportion of organic affinity is higher (50%) while silicate association is lower (50%).

In 21 Chinese coals of different rank (from lignite up to anthracite), in addition to aluminosilicate association ( $R(V-Al) = +0.42$ ), siderophile affinity was also observed ( $R(V-Fe) = +0.55$ ). As relationship with S was quite low ( $R(V-S) = +0.21$ ), it was concluded that V was bound in other Fe-bearing minerals than sulphides/disulphides (Liu et al., 2016). Siderophile character of V was mentioned also in other papers (Vassilev et al., 2005; Wagner and Hlatshwayo, 2005). The decrease in the proportion of organic affinity with increasing rank observed by Liu et al. (2016) agrees with the conclusion of Finkelman et al. (2018).

The results of Finkelman et al. (2018) are based on evaluation of 20 USGS coal samples from Australia, Great Britain, Canada, Brazil, and the USA (Pennsylvania, West Virginia, Kentucky, Alabama, Wyoming etc.) and were obtained by sequential leaching (discussed with the view of other available data, such as optical petrography, SEM with ED XRF, electron microprobe analysis, ion probe analysis, XRD or density fractionation). In case of Kentucky #9 and Illinois #6 coals, X-ray absorption spectroscopy data are available (Maylotte et al., 1981; Huggins and

Table 2

V concentrations (in ppm or µg/g) in coal gangue, rejects, waste materials co-combusted with coal and limestones.

| Material   | Details  | Concentrations              | Ref.                                  |                      |
|--|--|-----------------------------|---------------------------------------|----------------------|
| Coal gangue  | Coal gangue from Guqiao Coal Mine, China                                 | 54.3                        | (Zhou et al., 2014a)                  |                      |
|  | World coal gangue  | 100–400                     | (Zhou et al., 2014b)                  |                      |
|  | Clarke value-coal gangue   | 135                         | Zhou et al. (2014b)                   |                      |
| Coal gangue  | Huainan Coalfield China  | 10.1–83.1 (average 49.5)    | (Zhou et al., 2014b)                  |                      |
|  | Coal gangue  | 77                          | (Querol et al., 2008)                 |                      |
|  | Fired gangue (Coal)  | 88 (34)                     | Querol et al. (2008)                  |                      |
| Coal processing wastes   | Coal wastes from dumps   | 203–295 (average 243)       | (Ciesielczuk et al., 2014)            |                      |
|  | Coal pulveriser rejects  | From < 1% S coal            | 16 (ppm of ash)                       | (Hower et al., 2005) |
|  |  | From 1% to 2% S coal        | 46 (ppm of ash)                       | Hower et al. (2005)  |
| From > 3% S coal   |  | 55 (ppm of ash)             | Hower et al. (2005)                   |                      |
| Coal inclusions  | Coal inclusions  | 640 <sup>a</sup>            | (Yudovich, 2003)                      |                      |
|  | Bed coals  | 150 <sup>b</sup>            | Yudovich (2003)                       |                      |
|  | Raw/washed coals   | 46.5/16.3                   | (Quick and Irons, 2002)               |                      |
| Raw/washed coals   | G. Wood, UK  | 24.5/7.75                   | Quick and Irons (2002)                |                      |
|  | Correjon, Colombia   | 50.9/33.9                   | Quick and Irons (2002)                |                      |
|  | Harworth, UK   |                             | Quick and Irons (2002)                |                      |
| Petcoke  | Petcoke  | 1560                        | (Mukherjee et al., 2003; Sloss, 2007) |                      |
|  | Petcoke from petroleum refinery  | 586–1237                    | (Font et al., 2010)                   |                      |
|  | Coal (70%)/Petcoke (30%) feed blend                                      | 7950 (ash basis, 11.3% ash) | (Silva et al., 2013)                  |                      |
| Agricultural biomass   | Schlams/coal slurry/petcoke (2:7:1)                                      | 442                         | (George et al., 2008)                 |                      |
|  | World reference plant  | 0.5 <sup>c</sup>            | (Vassilev et al., 2014)               |                      |
|  | Clarke for angiospermous plants worldwide                                | 1.6                         | (Vassilev et al., 2014)               |                      |
| Clarke for gymnospermous plants worldwide                                | Clarke for gymnospermous plants worldwide                                | 0.69                        | Vassilev et al. (2014)                |                      |
|  | Peanut shell   | 2.81                        | (Zhou et al., 2014a)                  |                      |
|  | Wheat straw  | 7.17                        | Zhou et al. (2014a)                   |                      |
| Soybean stalk  | Soybean stalk  | 1.15                        | (Zhou et al., 2015)                   |                      |
|  | Corn stalk   | 2.92                        | (Zhou et al., 2016)                   |                      |
|  | Sawdust  | 2.64                        | Zhou et al. (2016)                    |                      |
| Wood pellets   | Wood pellets   | ca. 2 (from graph)          | (Guo and Zhong, 2018)                 |                      |
|  | Straw  | 2.24                        | (George et al., 2010)                 |                      |
|  | Waste wood   | 10                          | (Mukherjee et al., 2003; Sloss, 2007) |                      |
| Biomass mix (green wood, garden waste, straw, roadside grass and manure) | Biomass mix (green wood, garden waste, straw, roadside grass and manure) | 6                           | Mukherjee et al. (2003); Sloss (2007) |                      |
|  | Coal-Biomass feed blends   | 44.3 (3:1)                  | (George et al., 2008)                 |                      |
|  | Coal slurry – dry saw dust (3:7)   | 90.4                        | George et al. (2008)                  |                      |
| Coal-undried bark (1:3)  | Coal slurry – dry saw dust (3:7)   | 139                         | George et al. (2008)                  |                      |
|  | Coal-undried bark (1:3)  |                             | George et al. (2008)                  |                      |
| Sludge   |  |                             |                                       |                      |

Table 2 (continued)

| Material           | Details                 | Concentrations       | Ref.                                  |
|--------------------|-------------------------|----------------------|---------------------------------------|
| Paper sludge       | Paper sludge            | 5                    | (Mukherjee et al., 2003; Sloss, 2007) |
|                    | Municipal sewage sludge | 24                   | Mukherjee et al. (2003); Sloss (2007) |
| Sewage sludge      | Sewage sludge           | 15.61                | (George et al., 2010)                 |
|                    | Limestone               | 3 High-Cl limestones | 1.3, 5.8 and 15.1                     |
| Limestone          | Limestone               | 11                   | (Córdoba et al., 2012)                |
|                    | Limestone slurry        | 8                    | Córdoba et al. (2012)                 |
| 2 Czech limestones | 2 Czech limestones      | < 2.1                | (Klika et al., 2001)                  |

<sup>a</sup> Ash from the coal inclusions

<sup>b</sup> Ash from the bed coals

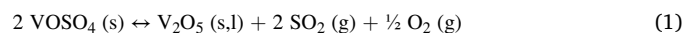
<sup>c</sup> Worldwide average of all parts of plants

Huffman, 1996, 2004; Huggins et al., 2009, 1997) and agree with the aforementioned sequential extraction ones (Finkelman et al., 2018).

The XAFS results are consistent – revealing two different V associations in coal – mineral and maceral association. The former is attributed to aluminosilicate affinity, probably with V-rich muscovite  $K(V^{3+}, Al)_2AlSi_3O_{10}(OH)_2$  (roscoelite) or illite containing  $V(3+)$ . In both these cases,  $V(3+)$  prevails (Huggins and Huffman, 1996; Huggins et al., 1997). In organic (maceral) association,  $V(4+)$  is more common than  $V(3+)$  that dominates in aluminosilicates (Maylotte et al., 1981; Huggins and Huffman, 2004). It was hypothesized that maceral association of V relates to poorly crystalline oxide  $V_2O_4$  or oxyhydroxide  $VO(OH)_2$  species (Huggins and Huffman, 2004).

### 3. Thermodynamic equilibrium calculations

Under standard oxidizing conditions and lower temperatures (below 630 K), according to Frandsen et al. (1994), vanadyl sulfates are formed. At ca. > 630 K,  $VOSO_4(s)$  decomposes to  $V_2O_5(s,l)$  according to Eq. (1) (Frandsen et al., 1994):



Between 1350 and 1645 K,  $V_2O_5(s,l)$  is converted to  $VO_2(g)$  (which is stable at 1640 K) according to Eq. (2) (Frandsen et al., 1994):



Under reducing conditions, V also forms O-species but  $V_2O_5(s,l)$  is converted to  $VO_2$  at 1500–1750 K, i.e. at higher temperatures (Frandsen et al., 1994).

As the only gaseous form of V in these equations is  $VO_2$ , it could be deduced that at oxidizing conditions V is more volatile than at the reducing ones, which is in agreement with the conclusion of Yan et al. (2001a) that unlike many other trace elements (Mn, Sb, Zn etc.), only V, As and Sn exhibited increased volatility under oxidizing conditions (vs. reducing ones), whatever the coal type (i.e., in both high-ash and low-ash coals). In this study, the difference in temperature for the same V volatility in oxidizing and reducing conditions was ca. 100 °C as well. It also agrees with the conclusions of Duchesne et al. (2018) that in combustion systems V is more volatile than in gasification ones. As higher oxidation states of V (that are more toxic) are expected during combustion (vs. gasification), it might result also in environmental consequences.

According to Yan et al. (2001b), V belongs to elements with high affinity to O, which has the order:

As > Se (Co, Cr, Mn, Pb, Sb, Te, V) > Ni > Sn > Zn > > (Cu, Hg) > other trace elements (Cd, Tl).

V forms O-combined species even at low mole fraction of O ( $O \approx 0.16$ ); with increasing amount of O, more V-O species appeared. The

most abundant are V-Ca (or Fe) oxides, such as  $\text{FeV}_2\text{O}_6$  (s),  $\text{CaV}_2\text{O}_6$  (s),  $\text{CaV}_2\text{O}_7$  (s),  $\text{Ca}_3\text{V}_2\text{O}_8$  (s),  $\text{FeV}_2\text{O}_4$  (s), etc. (Yan et al., 2001b). It is consistent with V species predicted by George et al. (2008, 2010) –  $\text{VO}_2$ ,  $\text{V}_2\text{O}_5$ ,  $\text{FeO}\cdot\text{V}_2\text{O}_5$ ,  $\text{CaO}\cdot\text{V}_2\text{O}_5$ , and  $2\text{CaO}\cdot\text{V}_2\text{O}_5$ . Predicted formation of  $\text{V}_4\text{O}_{10}$  was not observed experimentally, which was explained by kinetic constraints.

In addition to the effect of oxidizing or reducing atmosphere, there is also an effect of the rest of the atmosphere, which means that not only %  $\text{O}_2$  but also traditional (conventional) or *oxy-fuel atmosphere* could have an effect on V volatility (Jano-Ito et al., 2014). The comparison of temperatures where more than 50% V was volatilized revealed that this temperature was lower at air-fired combustion ( $> 660\text{ }^\circ\text{C}$ ) than at oxy-fuel combustion with 55.9% and 72.1% gas recycling ( $> 690\text{ }^\circ\text{C}$  and  $> 670\text{ }^\circ\text{C}$ ). However, this difference was not attributed to replacement of  $\text{N}_2$  by  $\text{CO}_2$ ; rather, it was explained by larger concentration of S (due to gas recycling) that binds Ca leaving its lower amount available for the formation of Ca-V oxides which results in more abundant  $\text{V}_2\text{O}_5$  formation (Jano-Ito et al., 2014). V interacts also with Cl, the temperature of  $\text{VOCl}_3$  occurrence is lower at oxy-fuel combustion ( $100\text{--}200\text{ }^\circ\text{C}$ ) than at air-combustion (ca.  $500\text{ }^\circ\text{C}$ ) (Jano-Ito et al., 2014).

#### 4. V in ash and slag wastes

##### 4.1. Concentrations of V in bottom ash (BA)/slags, fly ash (FA) and desulphurization residues

World averages for V concentrations in brown-coal and hard-coal ashes are 140 and 170 ppm (Ketris and Yudovich, 2009). V concentration ranges in FAs from Australia, Europe, and Canada-USA are 49–274 (median 143) ppm, 154–514 (median 202) ppm and 49–3120 (median 413) ppm, respectively (Riley, 2007; Sloss, 2007).

Elevated V content was observed in industrial FA originated from co-combustion of coal, tire-derived fuel and petcoke (1400 ppm) (Hower et al., 2001); extremely high concentration of V in FBC FA was obtained if petroleum coke was used as input fuel – 5473 ppm V (González et al., 2009). Co-combustion of coal and solid recovered fuel (SRF) containing plastics, wood, paper, fabric, rubber etc. produced FAs with V levels similar to those of conventional coal combustion – FAs from hard coal and SRF contained 103 and 175 ppm V (Wasielowski et al., 2020) or 353 ppm (Wojtaszek et al., 2021), FA originated from lignite and SRF contained 233 ppm V (Bartoňová et al., 2010). World reference for biomass ash (calculated as worldwide average for all parts of all plants and 4.9% ash yield) is 10 ppm (Vassilev et al., 2010, 2014); Clarke value for plant ash is 61 ppm V (Vassilev et al., 2014). V concentrations in desulphurization products have been published in literature as well. European (mostly from Germany), Japanese, and USA FGD gypsums contained 8–16, 21 and 10–12 ppm V, respectively (Berland et al., 2003; Sloss, 2007). V concentrations in FGD sulfate and sulfite were 8 and 15 ppm (Hower et al., 2005); in gypsum and gypsum slurry it was 7 and 5 ppm V (Córdoba et al., 2012). All these values are substantially lower than V contents in ashes or slags (mentioned above).

There are abundant papers reporting V concentrations in BA, slag, and FA samples from coal (co-) combustion; typically, V levels in FAs are moderately higher than those in BAs/slugs (and than those in coals). Fig. 2 depicts *enrichment factors* (EF) of V in FA compared to BA/slag (within the same combustion unit) and it was created using the literature data (top to bottom) (Font et al., 2010; Silva et al., 2010; Dahl et al., 2009; Silva et al., 2014; Parzentny and Róg, 2020; Córdoba et al., 2012; Querol et al., 1995; Tang et al., 2013; Hower et al., 1996; Wu et al., 2019; Chen et al., 2019; Karayigit et al., 2007; Spears and Martinez-Tarrazona, 2004; Silva et al., 2010; Chen et al., 2019; Narodoslawsky and Obernberger, 1996).

In most combustion tests, EFs are  $> 1$  indicating V enrichment in FA vs. BA/slag. The only exceptions are two white columns (Narodoslawsky and Obernberger, 1996; Chen et al., 2019) related to grate-fired units; the lowest value in the whole diagram (Narodoslawsky and

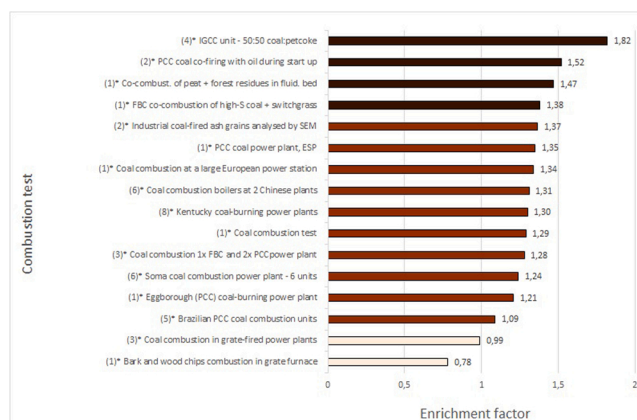


Fig. 2. Enrichment factors of V in FA vs. BA/slag. \*Numbers in parentheses indicate the number of FA-BA/slag pairs evaluated (and averaged).

Obernberger, 1996) relates to the test operating without coal – therein, only bark and wood were combusted in grate-fired facility. In contrast, it is interesting that the 4 highest EFs relate to units operating with coal and other materials, such as petcoke (EF=1.82) (Font et al., 2010), oil (EF = 1.52) (Silva et al., 2010), forest residue (EF = 1.47) (Dahl et al., 2009), or switchgrass (EF = 1.38) (Silva et al., 2014). Enrichment factors for normal PCC or FBC of (sole) coal are within the range of 1.09–1.37; despite combusting different types/ranks of coal in various units, the EF values are quite similar.

Due to  $\text{CO}_2$  neutral conversion and climate change benefits, the replacement of certain part of coal (gangue) by biomass during the combustion is intensively studied (Zhou et al., 2014a, 2015, 2016; Guo and Zhong, 2018). General conclusion of all these studies is decreased V percentage in FA (vs. BA) during combustion due to adding biomass. Even if V percentages of gaseous emissions remained low (ca. 1–2%) during combustion of coal gangue and soybean stalk, peanut shell, or sawdust (or their blends with the gangue), V proportion in BA during combustion of sole biomass was always higher than that in sole gangue – in case of soybean stalk and sawdust by ca. 5–10%, in case of peanut shell even by ca. 25%. Although the effect of the overall distribution of the ash particles during the combustion experiment cannot be neglected, higher levels of alkali and alkali earth elements were supposed to play a dominant role (Zhou et al., 2014a, 2015). Co-combustion of anthracite with wood pellets in fluidised bed have led to similar conclusion – adding wood pellets inhibit volatilization of V (Guo and Zhong, 2018).

##### 4.2. Distribution of V within ESP/baghouse rows

V concentrations in 3 (or more) rows of the same ESP or baghouse are for various combustion tests shown in Fig. 3. The diagram was created using the literature data (left to right) (Mardon et al., 2008; Tang et al., 2013; Santos et al., 2022; Santos et al., 2022; Santos et al., 2022; Santos et al., 2022; Kostova et al., 2016; Kostova et al., 2016).

V levels in these FAs are mostly a few hundred ppm, only in some individual cases they exceed 400 ppm. In most combustion tests, V levels gradually increase with increasing number of the row (i.e., in the last rows its content is typically higher). FA from the last rows contain more V; hence, such last-row ashes should be more suitable when searching for the cheap V source; nevertheless, amount of FA collected at the 3rd or later rows is rather low in comparison with FA from the 1st row which is more abundant.

This general trend (V increase in later rows FAs) is valid also for co-combustion of 70% pulverized coal + 30% pet coke (in Kentucky power station) (Silva et al., 2013). FA from the 1st row was not evaluated (due to difficulties with the FA collection), in the 2nd and the 3rd sections the V levels were 30,800 ppm and 35,600 ppm V – these concentrations are high due to high V content in 70% coal/30% petcoke feed fuel – 7,

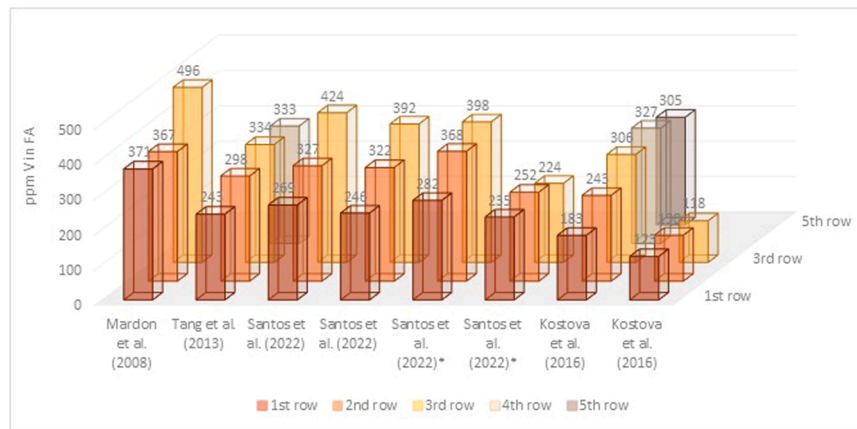


Fig. 3. Concentrations of V in individual rows of ESP or baghouse filters. \*Values plotted herein for the 3rd row are in fact mixtures of the 3rd and the 4th row FAs.

950 ppm (ash basis; 11.3% ash). Increasing concentration of V (and other pollutants) (Czech et al., 2020) with decreasing particle size of FA is undesirable from environmental point of view because the finest PM particles can be distributed to large surrounding areas releasing toxic pollutants there (Kantor et al., 2021; Švédová et al., 2019).

#### 4.3. Influence of combustion procedure and operating parameters

Relative enrichment (RE) of V in FA (vs. coal) compared for 3 types of industrial combustion units with grate fired, pulverized coal and fluidised bed boilers revealed moderate increase in RE in FA in the order: grate-fired boiler (700 °C) < pulverized coal boiler (1400 °C) < fluidised bed boiler (950 °C) – all these values ranged from ca. 0.7 to ca. 0.8 documenting in all cases V depletion in FA vs. coal (Chen et al., 2019). Apart from the effect of the different V associations in the studied coals, interestingly, this sequence did not follow the combustion temperature increase that was in the different order: grate-fired boiler (700 °C) < fluidised bed boiler (950 °C) < pulverized coal boiler (1400 °C). Since V is not a typical volatile element and generally tends to remain in condensed fractions, it might rather reflect the overall redistribution of mineral matter. Another possible effect relates to unburned carbon levels in these three industrial ashes because the RE value was calculated according to the traditional formula:

$$RE = \frac{(c_i)_{ash}}{(c_i)_{coal}} \cdot \frac{(\%ash)_{coal}}{100}$$

where  $c_i$  are the concentrations of the  $i$ -th elements (herein of V) in ash and coal. The  $(\%ash)_{coal}$  relates to the ash content in the coal and 100 in the denominator is used for the approximate ash content in the evaluated ash or slag. Even if unburned carbon levels in these samples were not published (Chen et al., 2019) it can be presumed that unburned carbon levels (generally) decrease in the order: grate fired boiler > pulverized coal boiler > fluidised bed boiler. Hence, as the RE differences among the boiler types are quite low (0.7–0.8) it could be hypothesized that high unburned carbon levels in the ash could “dilute” V contents there leading to moderately lower RE values (in comparison with RE in the ash containing negligible amount of unburned carbon).

The comparison of industrial combustion and household stove combustion (Pędziwiatr et al., 2021) led to the conclusion that ash and soot samples from the household stoves contained lower V concentrations (< 92 ppm) in comparison with industrial BA and FA samples (140–248 ppm), probably due to wood that was co-combusted with bituminous coal in household stove (co-combustion of wood or other biomass types with coal is quite common practice) (Růžičková et al., 2019b).

#### 4.3.1. Oxy-fuel combustion and effect of water

**Oxy-fuel combustion.** As coal combustion is an important contribution to anthropogenic greenhouse gas (CO<sub>2</sub>), modern technologies mitigating CO<sub>2</sub> emissions are intensively studied (Mikulčić et al., 2022). One of the most feasible options in the mid-term horizon is oxy-fuel combustion (Senneca et al., 2017). In comparison with traditional air-combustion, coal is burned usually in a mixture of oxygen and recycled flue gas, which enables to attain high CO<sub>2</sub> concentration in exhaust gas (Davidson and Santos, 2010).

Experimental results of co-combustion of bituminous coal and sawdust under air (21%O<sub>2</sub>/79%N<sub>2</sub>) and oxy-fuel combustion conditions (21%O<sub>2</sub>/79%CO<sub>2</sub>) revealed practically no effect of changed atmosphere. Zhou et al. (2020) observed nearly the same ratios of V in FAs at both atmospheres for 800 °C, 900 °C, and 1000 °C combustion experiments (ca. 40–48% according to the temperature); the volatilization ratios remained also unchanged - in both atmospheres it was 2–3%. In the study of Oboirien et al. (2014), the V concentrations in 900 °C BAs generated at 21%O<sub>2</sub>/79%N<sub>2</sub> and 21%O<sub>2</sub>/79%CO<sub>2</sub> atmospheres were exactly the same. The results of Jano-Ito et al. (2014) (described in detail in Section 3) and Zhou et al. (2020) or Oboirien et al. (2014) are quite similar; nevertheless, moderately lower V volatility under oxy-fuel combustion conditions (vs. air combustion) concluded by Jano-Ito et al. (2014) was not observed by Zhou et al. (2020) and Oboirien et al. (2014). This minor difference might be brought about by mixing pure gases by Zhou et al. (2020) and Oboirien et al. (2014), while Jano-Ito et al. (2014) recycled the whole flue gas including S, Cl, H<sub>2</sub>O etc.; the elevated concentrations of S, Cl, and H<sub>2</sub>O might result in minor decrease in V volatility.

In addition to oxy-fuel combustion, there are also other promising technologies with environmental benefits, such as IGCC (combined optimally with CO<sub>2</sub> capture) (Ordorica-Garcia et al., 2006), co-firing with low C or C-neutral fuels (biomass (McIlveen-Wright et al., 2007), H<sub>2</sub> or ammonia (Xu et al., 2022) or waste-derived fuels (Mikulčić et al., 2016)) or carbon capture technologies (e.g., chemical looping combustion using particulate solid oxygen carrier (Coppola and Scala, 2021) or using mineral carbonation technology (Coppola et al., 2022)). As V behaviour and the ash characteristics are expected to be different and highly variable, more research attention is needed in this field.

**Effect of water.** Effect of water (moisture) on behaviour of trace elements is generally more pronounced in case of oxy-fuel combustion due to flue gas recycling (thereby increasing levels of H<sub>2</sub>O) (Roy et al., 2013) or if coal-water slurry is combusted (Vershina et al., 2016, 2020; Glushkov et al., 2016). When waste materials containing higher moisture levels are co-combusted with coal, such as sewage sludge, agricultural or forest residues – then different drying methods might also have certain effect (Raclavska et al., 2011; Tun and Juchelková, 2019b).

Papers on effect of water (e.g., during coal water slurry combustion)

on behaviour of elements are extremely scarce or nearly non-existent. In case of Cr, Mn, and Ni, the bottom emission stream was higher in coal-water slurry fuel than in case of pulverized coal combustion, which was attributed to lower temperatures during coal-water slurry fuel combustion and possibly also due to larger agglomerates formed from coal-water droplets (Nodelman et al., 2000). Nevertheless, V was not included in this study. Increase of H<sub>2</sub>O content in MSW from 0 to 65 wt% during the pyrolysis at 650 °C led to increase of V content in solid phase (by ca. 4 mg/kg) while its levels in oil and liquids remained low (< 1 mg/kg) and nearly the same regardless the water level (Raclavská et al., 2015). Results from two multi-burner coal-water slurry gasification plants (with ca. 60 wt% coal in slurry containing 9.1 and 9.6 ppm V) revealed lower V levels in coarse slags (114 and 116 ppm V) and higher V levels in fine slags (152 and 155 ppm V) (Jiang et al., 2021).

Higher water levels influence also the catalytic effect of V<sub>2</sub>O<sub>5</sub> on oxidation of SO<sub>2</sub> to SO<sub>3</sub> during coal combustion – higher H<sub>2</sub>O levels increase the formation of SO<sub>3</sub>; the most effective catalyst was V<sub>2</sub>O<sub>5</sub> while Fe<sub>2</sub>O<sub>3</sub> and CuO exhibited somewhat lower effect (Duan et al., 2015).

Moreover, according to Galetz (Galetz, 2015), combined effect of low-quality fuels containing high V concentrations (oil sands, refinery residues etc.) and reducing atmosphere with high levels of CO, water and H<sub>2</sub>S can accelerate the corrosion of boilers or heat exchangers if made from low Cr steel.

#### 4.3.2. Combustion additives

Silica-based additive used for the inhibition of ash slagging and fouling (Low et al., 2015) in industrial pulverized coal-fired boiler (1300 °C) provided noticeable reduction in enrichment across all boiler positions not only for V but also for As, Cr, and Mn. Addition of the silica-based additive slightly increased the tendency of V to remain in the gas phase. Thermodynamic equilibrium predictions on V states during coal combustion at 1300 °C revealed significant increase of gaseous (VO<sub>2</sub>) fraction if silica-based additive was added. In both cases (with or without silica-based additive), the most abundant solid phase was (CaO)<sub>3</sub>(V<sub>2</sub>O<sub>5</sub>). Formation of Ca-V species has been mentioned also in other studies (Folgueras et al., 2007; Díaz-Somoano et al., 2006) which could be important in terms of using traditional Ca-bearing additives (limestone, dolomite, lime etc.). Calcium vanadium oxide hydrate (Ca<sub>2</sub>V<sub>2</sub>O<sub>7</sub> · 2 H<sub>2</sub>O) was identified also in ash from fluidised bed combustion of 100% petcoke where limestone was used as desulphurization additive (Jia et al., 2002). However, in FBC (850 °C) the correlation coefficients V-Ca in BAs from 4 combustion tests with CaCO<sub>3</sub> or CaO added to bituminous coal or lignite were in all cases negative (R was from –0.3 to –0.5) (Bartoňová and Klika, 2014), which is in agreement with the literature results described in the next section (Bielowicz, 2020; Spears and Martínez-Tarrazona, 2004; Singh et al., 2011; Huggins and Huffman, 1996; Huggins et al., 1997). Therefore, it could be hypothesized that synergetic effect of more factors leads to the formation of Ca-V compounds. The effect of Ca-bearing minerals (in this context) is probably enhanced by organic or other volatile V association in the fuel (coal, petcoke etc.). And, the effect of the combustion temperature is important as well because if V is firmly bound in aluminosilicates, low combustion temperature (e.g., in fluidised bed combustion) is not sufficient for V volatilization thereby hindering its interaction with Ca-bearing additives.

#### 4.4. V speciation in ash and slag wastes

As mentioned in Section 2.2., V in coal is associated predominantly with aluminosilicates and organic matter (macerals) (Finkelman et al., 2018; Maylotte et al., 1981; Huggins et al., 2009).

Relationships of V with major elements in coal ashes were evaluated (i.a.) by Singh et al. (2011), Spears and Martínez-Tarrazona (2004) or Bielowicz (2020). Correlation coefficients calculated for V-Al<sub>2</sub>O<sub>3</sub> relationship in coal ash by Singh et al. (2011), Spears and

Martínez-Tarrazona (2004) and Bielowicz (2020) were + 0.89, + 0.54 and + 0.40, respectively. Despite quite big differences in these values, all these three R values are statistically significant. As critical value of correlation coefficient (for 2-tailed probability) decreases with the increase of the number of evaluated data, the critical value for the 9 measurements of Singh et al. (2011) is 0.798 ( $\alpha = 0.01$ ) or 0.666 ( $\alpha = 0.05$ ), for the data of Spears and Martínez-Tarrazona (2004) it is 0.39 ( $\alpha = 0.01$ ) and for the 28 samples of Bielowicz (2020) it is 0.374 ( $\alpha = 0.05$ ). These results document at least partial association of V with aluminosilicates in the studied coal ash samples. Moreover, high R(V-K) calculated by Spears and Martínez-Tarrazona (2004) is also consistent with previously published V association with illite or roscoelite in coal (Huggins and Huffman, 1996; Huggins et al., 1997). In some FAs, siderophile character of V has also been observed. In Eggborough FA, Spears and Martínez-Tarrazona (2004) based this conclusion on the correlation coefficient calculation where  $R(V-Fe) = +0.61$  (critical value for  $\alpha = 0.01$  is 0.39), while Vassilev and Menendez (2005) based it on V enrichment in heavy-mineral fraction (heavy concentrate with  $\rho > 2.89 \text{ g/cm}^3$ ).

Unlike ashes originated from coals, BAs prepared at 500 °C (2 h) from 8 biomass samples (beech wood chips, corn cobs, marine macroalgae, weathered plum pits, rice husks, switchgrass, sunflower shells, and walnut shells) did not reveal significant association of V with silicates or Fe (Vassilev et al., 2014). In contrast to coal ashes, V exhibited the affinity to chlorides, sulphates, Na, Cr, Sr, U, and Ni. The strongest association was observed with S ( $R^2(V-S) = 0.99$ ) (Vassilev et al., 2014).

In co-combustion of pulverized coal (70%) and petcoke (30%), the XPS binding energy of V was primarily attributed to V(5+) (Vassilev et al., 2014). HR-TEM/EDS/SAED documented (in FA) multiwalled nanotubes encapsulating V. In ultrafine particles, V-spinels were incorporated into the magnetite structure (replacing Fe<sup>2+</sup> and Fe<sup>3+</sup> ions in crystal lattice) (Silva et al., 2013). It could correspond with quite high R(V-Fe) = +0.61 (statistically significant value for  $\alpha = 0.01$  is 0.39) in Eggborough PCC FA (Spears and Martínez-Tarrazona, 2004). Results presented by Izquierdo et al. (2007) for 2 FAs from Spanish power plants document practically no effect of % petcoke added to coal during co-combustion on V speciation – in both FAs (4% and 24% petcoke), the prevalent form of V was vanadate VO<sub>4</sub><sup>3-</sup> with minor proportion (<30%) in lower oxidation states (mainly V(4+)). In contrast, the effect of combustion/gasification atmosphere on V speciation is more significant (Duchesne et al., 2018). Synchrotron-based XAS revealed that petcoke gasification products contain 79–95% V(3+) and the rest is V(4+) while combustion products contain 40–71% V(5+) and 12–60% V(4+) (Duchesne et al., 2018), NaVO<sub>3</sub> (Bacci et al., 1983) and vanadyl sulphate (Huffman et al., 2000) were identified at oil-fired power plants.

Details on V speciation are important not only in terms of toxicity or possible V extraction. There is also an effect on corrosion and fouling of combustors that is attributed mainly to V(5+) while V(4+) and V(3+) are considered innocuous (Duchesne et al., 2018).

## 5. Physical separation

Physical separation methods the most widely applied on coal combustion wastes are particle-size fractionation, magnetic separation, density separation, flotation, electrostatic separation etc.

### 5.1. Particle-size fractionation

In case of 2 industrial coal combustion FAs (390 and 270 ppm V), the highest V concentrations within particle size fractions were observed in < 25  $\mu\text{m}$  fractions (480 and 320 ppm V) (Hower et al., 1999). The finest and the coarsest fractions of FA (with bulk 507 ppm V concentration) contained 1236 and 227 ppm V (Lanzerstorfer, 2018); particle-size fraction of another coal FA (with 496 ppm V) revealed the enrichment of V in the finest fraction (596 ppm V) and the depletion in the coarsest one (120 ppm) as well (Mardon and Hower, 2008). Size fractionation

applied on the non-magnetic residue of coal FA (after magnetic separation) is also consistent with the aforementioned trend – the highest V concentration (435.9 ppm) was obtained in the finest fraction, the coarsest fraction contained substantially lower V content (136 ppm) (Querol et al., 1995). The same particle-size distribution trend in FA was observed even if peat was co-combusted with forest residues in fluidised bed boiler (the highest V content 150 ppm V relates to < 0.074 mm fraction). In this fraction, around 94% of V was present. In BA, the highest level of V was in 0.25–0.5 mm fraction (also ca. 150 ppm) and it decreased with increasing particle size to below ca. 20 ppm V (Dahl et al., 2009).

Overall, literature data on particle-size distribution of V in FA provide a clear and consistent trend – enrichment of V in the finest FA fractions.

## 5.2. Magnetic separation

Amount of magnetic concentrate separated from FA mostly fall within the range of 0.5%–18.1% (Vassilev et al., 2004). The most abundant magnetic minerals present in magnetic fractions are magnetite, hematite, ferrian spinel, Ca- and Ca-Mg spinels with some minor occurrence of maghemite, martite, musketoite, wustite, ilmenite, chromite, native Fe, Mn ferrite, ferrosilicon, Fe hydroxides and Fe silicates (Vassilev et al., 2004) (and the references therein).

Comparison of V levels in magnetic and non-magnetic fractions are summarized in Table 3. Results summarized in Table 3 are quite inconclusive: there are samples exhibiting V enrichment in magnetic fractions (Santos et al., 2022; Cornelius et al., 2021), in non-magnetic fractions (Querol et al., 1995) or showing no clear trend (Vassilev et al., 2005; Strzałkowska, 2021; Myazin et al., 2018). These differences could be brought about by different association of V in coal combustion wastes and/or by different separation techniques used in evaluated papers.

According to Myazin et al. (2018), approximate minimum commercial content of a valuable component for V is 500 g/t (ppm or µg/g). Comparing this value with data in Table 3, the only magnetic concentrate meeting this requirement is magnetic fraction prepared from heavy

concentrate of the only 1 FA sample (656 ppm V on air-dried basis) (Vassilev et al., 2005). It is worth mentioning in this context that another FA from the same thermal power station treated in the same way provided only 273 ppm V – which clearly documents the effect of input coal (ash) characteristics (Vassilev et al., 2005). Quite high V levels were reported also by Santos et al. (2022) for 2 magnetic concentrates of 2 ESP FAs – 420 and 372 ppm V. Enrichment factor calculated for V concentration in magnetic concentrate (vs. bulk FA) for 5 Spanish FAs was 1.0 showing no enrichment (Vassilev et al., 2004).

Therefore, the combination of more methods is generally needed if greater enrichment is required.

## 5.3. Density separation

Density fractionation from slag (155.2 ppm V) and FA (208.3 ppm V) from the same power station provided the highest V content (160 ppm) in 2.4–2.8 g/cm<sup>3</sup> fraction of slag and 2.4–2.8 g/cm<sup>3</sup> fraction of FA (229.9 ppm V), which could be given by prevalent aluminosilicate affinity in these samples (Querol et al., 1995).

Average concentration of V in 5 heavy concentrates prepared by sink-float technique in bromoform ( $\rho = 2.89 \text{ g/cm}^3$ ) from 5 FAs generated from 4 Spanish thermal power stations was 256 ppm. As average concentrations of V (ash basis) in these original FAs were 201 ppm, V was enriched in heavy concentrates, which corresponds with predominant siderophile character (Vassilev and Menendez, 2005).

## 5.4. Char concentrates (from ash) and electrostatic separation

There are numerous procedures used for the separation of carbon concentrates from coal ash, such as triboelectrostatic separation, density separation, oil agglomeration, fluidization or vibrational separation etc. (Lv et al., 2022). Char concentrates separated manually (when dry) from two > 0.1 mm FAs provided 111 and 261 ppm V; the comparison with V levels in bulk FAs (266 and 316 ppm) indicates depletion of V in char from Turkish FAs (Vassilev et al., 2005). In 5 Spanish FAs, average V enrichment factor in carbon concentrates (vs. V content in bulk FAs) was 1.1 showing moderate enrichment.

**Table 3**

V concentrations (in ppm or µg/g) in magnetic and non-magnetic fractions of coal combustion ashes/slags.

| Combustion   | Separation   | Ash/slag                    | Magnetic fraction | Non-magnetic fraction              | Ref.                      |
|--|--|-----------------------------|-------------------|------------------------------------|---------------------------|
| 1050 MW European power station                     | Magnetic separator with ultrasonic bath (in acetone)         | FA (from bituminous coal)   | 227               | 237                                | (Querol et al., 1995)     |
|  |  | Slag (from bituminous coal) | 150               | 160                                |                           |
| PCC thermal power station                          | Dry separation   | FA1                         | 273 <sup>a</sup>  | 423 <sup>b</sup> /111 <sup>c</sup> | (Vassilev et al., 2005)   |
|  |  | FA2                         | 656 <sup>a</sup>  | 198 <sup>b</sup> /261 <sup>c</sup> |                           |
| Thermal power plant in Eastern Transbaikalia       | Laboratory magnetic separation at<br>i)10 kA/m<br>ii)30 kA/m | i)FA1                       | 70                | 60                                 | (Myazin et al., 2018)     |
|  |  | FA2                         | 5.0               | 20                                 |                           |
|  |  | ii)FA1                      | 60                | 60                                 |                           |
|  |  | FA2                         | 30                | 30                                 |                           |
| Power plants in Poland, bituminous coals           | Manual magnetic separator                                    | Slag 1                      | 182.9             | 272.6                              | (Parzentny and Róg, 2020) |
|  |  | Slag 2                      | 174.2             | 157.7                              |                           |
| Arnot power station (South Africa)                 | Wet separation in water                                      | FA                          | 126               | 119                                | (Cornelius et al., 2021)  |
| Energetic coal combustion (power plants in Poland) | Dry manual separation using magnet                           | Class F FA                  | 204               | 235                                | (Strzałkowska, 2021)      |
|  |  | Class C FA                  | 274               | 208                                |                           |
| PCC combustion at 1500 °C, Colombian coal          | Manual wet separation (ferrite magnet)                       | BA 1                        | 228               | 204                                | (Santos et al., 2022)     |
|  |  | Economizer ash 1            | 236               | 159                                |                           |
|  |  | ESP FA 1                    | 420               | 229                                |                           |
|  |  | BA 2                        | 205               | 192                                |                           |
|  |  | Economizer ash 2            | 229               | 166                                |                           |
|  |  | ESP FA 2                    | 372               | 239                                |                           |
|  |  | FA ESP 1st row              | 6159 <sup>d</sup> | 8188 <sup>d</sup>                  |                           |
| FA ESP 2nd row                                     | 5635 <sup>d</sup>  | 8079 <sup>d</sup>           | (Henke, 2005)     |                                    |                           |

<sup>a</sup> Magnetic fraction from heavy (> 1 g/cm<sup>3</sup>) fraction

<sup>b</sup> Light fraction (< 1 g/cm<sup>3</sup>)

<sup>c</sup> Char concentrate (manually separated from > 0.1 mm fraction)

<sup>d</sup> After ashing at 750°C



Electrostatic separation applied on 2 coal combustion wastes (at  $U = 10$  kV) provided for the first sample moderate enrichment in the conductors' fraction and enrichment in the dielectrics fraction for the second one. When  $U = 20$  kV was used, in case of both these samples, the highest V content was observed in the intermediate (semiconductors) fraction. Nevertheless, V content in none of these fractions did not exceed 200 ppm (Myazin et al., 2018).

Thus, overall, individual physical–separation techniques typically do not lead to significant V enrichment that could be sufficient for commercial utilization of coal combustion wastes as a cheap source of V. Therefore, the combination of these techniques is recommended optimally after evaluation of input fuel characteristics. Nevertheless, the “pre-concentrate” thereby obtained might become an advantageous input material for further application of chemical / biotechnological methods (that are discussed in detail in Section 6). And at the same time, such techniques could be used in order to decrease V levels in ashes/slugs. Utilization perspectives of fractions depleted in V (and other trace elements) in terms of their storage, handling, landfilling or further technological use are thereby better.

## 6. Chemical extraction from ash and slag wastes

Methods of elemental extraction from ash and slag wastes include the following approaches (Yermagambet et al., 2018; Vitolo et al., 2000; Ye et al., 2012):

- i) Acid leaching (of basic or amphoteric compounds using solutions of  $H_2SO_4$ , HCl etc.)
- ii) Alkali leaching (of acidic or amphoteric compounds using solutions of NaOH,  $NH_4OH$  etc.)
- iii) Extraction under severe conditions (high temperature and pressure, using aggressive chemicals, roasting etc.)
- iv) Biotechnology – leaching using microorganisms.

### 6.1. Leachability in water

In general, leached amount of elements in water is given by their concentration in ash, mode of occurrence in ash, operating conditions during combustion, adsorption/desorption processes, redox conditions and namely by pH (Vassilev et al., 2020).

V leachability in water from coal combustion ashes/slugs is generally low. Proportions of V leached from 9 Bulgarian coal FAs (by water) was within the range of 0.1–1.0% (Vassilev et al., 2020). Around 0.1–4% V water leachable fraction from coal FAs reviewed by Izquierdo and Querol (2012) is also quite low and consistent with other authors (Lieberman et al., 2020; Pires and Querol, 2004; Querol et al., 2000; Spears, 2013). However, co-combustion of coal with wastes or even the combustion of biomass without coal might substantially elevate water leachability of V. High V solubilities in water was obtained from biomass ashes (prepared at 500 °C for 2 h) where V was preferably associated with water-soluble fraction – sulphates and chlorides (Vassilev et al., 2014). Therefore, it is recommended to remove the water-soluble phases prior to such ash is used (Vassilev et al., 2014).

When low and high amount of petcoke was co-fired with coal (in large power station) (Izquierdo et al., 2007), increasing petcoke fraction added to coal increased the leachable content of V, not only absolutely (7 mg/kg and 190 mg/kg V in the leachates) but also relatively (1.8% from 380 mg/kg V in FA1 and 4.9% from 3890 mg/kg V in FA2). As it cannot be fully attributed to pH change ( $pH_1 = 8.1$  and  $pH_2 = 8.3$ ), rather, leachable amount reflects total V levels and probably also different modes of occurrence in low- and high- petcoke FAs (Izquierdo et al., 2007). The authors concluded that higher proportion of organically bound V (in 24% petcoke blend) somewhat hinders its assimilation to aluminosilicates thereby increasing its leachability in water. It is worth mentioning in this context that V concentration in the leachate

from high-petcoke FA is quite high (190 mg/kg) and might be potentially harmful (Izquierdo et al., 2007); therefore, extraction of V from such FA would be practical thereby enhancing its utilization options/possibilities.

### 6.2. Effect of pH

During the leaching, one of the most crucial affecting factors is pH; its effect on dissolved V concentration in the leachate is in some instances even more important than total V concentration in ash/slag (Silva et al., 2010). Literature results related to the effect of pH on V leachability from coal combustion ash and slag wastes are listed in Table 4.

The data summarized in Table 4 document that pH of the solution plays an important role in elemental mobility, which was in most studies the highest at  $pH \approx 2$  (Zhao et al., 2020; Zhang et al., 2019b; Stefaniak et al., 2018; Sandeep et al., 2016). In such studies, pH of the solution was adjusted by adding  $HNO_3$  (or NaOH). In the review paper by Izquierdo and Querol (2012), maximum V mobility was at  $pH = 7–11$  (from evaluated range of 4–14), which corresponds with moderately higher (local maximum) leaching of V in  $pH = 7–9$  in the study of (Zhao et al. (2020)).

Other studies evaluate V mobility in dependence of natural pH of the suspension ash/slag–water without any pH adjustment (Lieberman et al., 2020; Silva et al., 2010). In case of high-S and -Ca FAs, V mobility (in 24-h experiments) decreased with pH increase from 9.98 to 12.17 (Lieberman et al., 2020; Silva et al., 2010), which agrees with the conclusion of Nugteren et al. (2002) that due to Ca extraction, pH increases with time in longer experiments and it might result in re-precipitation of elements that have already been extracted at earlier stages. According to Izquierdo and Querol (2012), in higher-Ca systems, the formation of calcium vanadates is an important factor in terms of V solubility. This might be one of the reasons why some authors (Nugteren

**Table 4**  
The effect of pH on leachability of V from ash and slag wastes.

| Combustion  | Leaching  | results  | Ref.                     |
|---|---|--|--------------------------|
| 5 PCC FAs (4 ESP, 1 FF), sole coal  | US EPA LEAF 1313 test, $pH \approx 2–13$ ( $HNO_3$ -NaOH), L/S= 10                | Maximum V solubility at $pH \approx 2$ , high also at $pH \approx 7–9$ , the lowest at $pH \approx 4$ or 11–12   | (Zhao et al., 2020)      |
| 1FA (FF) + 1BA, CFB, alkaline coal  | US EPA LEAF 1313 test, $pH \approx 2–13$ ( $HNO_3$ -NaOH), L/S= 10                | Maximum V solubility at $pH \approx 2$ (FA and BA)   | (Zhang et al., 2019b)    |
| PCC co-firing with off gas fuel, class F FA of sialic type                  | US EPA LEAF 1313 test, $pH \approx 2–13$ ( $HNO_3$ -NaOH), L/S= 10                | Maximum V solubility at $pH \approx 2$ (FA from sole coal and from co-firing with off gas fuel)  | (Stefaniak et al., 2018) |
| 2 low-grade coal FAs, Indian power plants                                   | $pH \approx 2–12$ ( $HNO_3$ -NaOH), L/S= 20                                       | Maximum V solubility at $pH \approx 2$ (both FAs)  | (Sandeep et al., 2016)   |
| 7 high S and Ca coal FAs  | EU standard Batch Leaching Test EN 12457–2, L/S= 10 L/kg, 24 h, no pH adjustment) | Solubility of V decreases as pH increases from 9.98 to 12.27 (max at 9.98)   | (Lieberman et al., 2020) |
| 7 PCC units of the same power plant (7 ESP FAs, 5 normal + 2 oil co-firing) | EU standard Batch Leaching Test EN 12457–2, L/S= 10 L/kg, 24 h, no pH adjustment  | i)5 FAs from sole coal (less V in FAs): $pH 9.9–10.4$ , higher V mobility<br>ii)2FAs from oil co-firing (more V in FAs): $pH 5.3–6.2$ , lower V mobility | (Silva et al., 2010)     |

et al., 2002) recommend incorporation of a prewashing step with water prior to using the extraction agents – it leads to higher elements removal rates and/or lower reagent consumption; even prior to bioleaching procedures (Jadhav and Hocheng, 2015).

Natural pH of the leachate is affected by coal characteristics and by co-combustion of other materials with coal. Comparison of PCC FAs from oil co-firing with normal coal combustion FAs (collected at the same combustion unit) documents diametrically different V behaviour (Silva et al., 2010). Normal coal combustion FAs with low V levels provided alkaline (pH = ca. 10) leachate with higher V concentration in comparison with pH = ca. 6 and higher V concentrations in the leachates from oil co-firing FAs (Silva et al., 2010). These results were interpreted through different modes of occurrence of V in FAs/leachates during normal combustion and co-firing with oil because element in oxyanionic form is expected to be mobile under neutral and alkaline conditions while cationic species are mobile in acidic environments (Silva et al., 2010; Cornelis et al., 2008).

### 6.3. Acid leaching

Various acids can be used for V leaching from ash and slag wastes (e. g., HCl or HNO<sub>3</sub>) (Wang et al., 2004) but absolutely the most widely used is diluted H<sub>2</sub>SO<sub>4</sub>.

#### 6.3.1. Leaching by diluted H<sub>2</sub>SO<sub>4</sub>

Literature results on H<sub>2</sub>SO<sub>4</sub> leaching of coal FAs (and other related materials) are listed in Table 5. Many researchers use increased temperature for H<sub>2</sub>SO<sub>4</sub> leaching, such as 60–80 °C (Nazari et al., 2014; Chen et al., 2010) or 90 °C (Nazari et al., 2014; Chen et al., 2010); leachability of V can be improved also by using ultrasound (Masoum et al., 2021) or

**Table 5**  
Leached percentages of V (and other elements) during H<sub>2</sub>SO<sub>4</sub> leaching of FAs.

| Sample   | Procedure   | Leached percentages  | Ref.                  |
|--|---|--|-----------------------|
| Coal FA  | 1.5 M H <sub>2</sub> SO <sub>4</sub> , 25 °C, 3 h<br>500 g FA / 1 L leachant  | 21% V, 2.4% Ga, 60% B, 12% Cr, 25% Mn                              | (Tsuboi et al., 1991) |
| 3 lignite FAs  | H <sub>2</sub> SO <sub>4</sub> , pH ≈ 1, 25 °C, 14 days   | 57.4%, 72% and 86.6% V, ca. 80% Cd, Zn, U, Th, ca. 60% Cu, Co, Ni  | (Seferinoglu, 2003)   |
| i) 2 lignite ashes (294 and 265 ppm V)<br>ii) 1 wood ash (6 ppm V)<br>iii) 1 asphaltite ash (3990 ppm V) | 1 M H <sub>2</sub> SO <sub>4</sub> , S: L= 1:10, 10 days, pH ≈ 1  | i) 60% and 95%<br>ii) ≈ 100%<br>iii) below 80%                     | (Paul et al., 2006)   |
| Power plant FA   | i) 25% H <sub>2</sub> SO <sub>4</sub> , S: L= 7.5, 62.5 °C, 3 h<br>ii) 19.47% H <sub>2</sub> SO <sub>4</sub> , S: L= 9.15, 80 °C, 2 h                       | i) 99.89% V<br>62.56% Ni<br>ii) 94.28% V<br>81.01% Ni              | (Nazari et al., 2014) |
| Coal FA (50 ppm V, 11 ppm Y)   | 32.18% H <sub>2</sub> SO <sub>4</sub> , 15.67% H <sub>2</sub> O <sub>2</sub> , 90 °C, 1 h, S/L= 0.06%, ultrasonic bath                                      | 100% V<br>97% Y  | (Masoum et al., 2021) |
| Stone coal (1.09% V <sub>2</sub> O <sub>5</sub> )  | i) 6 M H <sub>2</sub> SO <sub>4</sub> , S: L= 1:3, 80 °C, 2 h<br>ii) 6 M H <sub>2</sub> SO <sub>4</sub> , S: L= 1:3, 90 °C, 3–5 h, 6% helping reagent       | i) 79.88% V<br>ii) 95.86% V  | (Chen et al., 2010)   |
| i) 3 Heavy oil FAs (1.3–3.3% V)<br>ii) 1 Orimulsion FA (11.7% V)   | i) 2 M H <sub>2</sub> SO <sub>4</sub> , boiling temperature, L/S= 3 mL/g<br>ii) 2 M (3 M) H <sub>2</sub> SO <sub>4</sub> , boiling temperature, L/S= 3 mL/g | i) 82%, 90% and 98% V <sub>a</sub><br>ii) 80% (95%) V <sub>a</sub> | (Vitolo et al., 2000) |

<sup>a</sup> rough estimation – data from graph

adding other reagents (e.g., H<sub>2</sub>O<sub>2</sub>) (Masoum et al., 2021; Chen et al., 2010). Even if extraction yields are quite variable (due to different ash/slag characteristics and the procedures used), in most cases it exceeds 95%. However, the extraction percentage should be evaluated in the context of bulk V content in the leached material; for example, 80% V leached from 3990 ppm in asphaltite ash provide more V than 100% recovery from wood ash with 6 ppm V (Paul et al., 2006).

Ashes provide better V extraction yields (when leached by H<sub>2</sub>SO<sub>4</sub>) than their coal counterparts (Seferinoglu, 2003) which is consistent with better V dissolution in 6% HCl and 6% HNO<sub>3</sub> out of ashes than original coals (Wang et al., 2004). It can be attributed to breakage of stable chelates of V porphyrins present in original fuel during the combustion (Paul et al., 2006).

It is practical from economic point of view if extraction procedure is slightly modified (thereby losing in some cases a few % in V yield) in order to extract within the same procedure also other elements, such as Y (Masoum et al., 2021) or Ni (Nazari et al., 2014). And vice versa – V can be “co-leached” during the H<sub>2</sub>SO<sub>4</sub> extraction of other elements, such as Ce or Ga; then the retention efficiency is naturally somewhat lower (Yermagambet et al., 2018).

However, radioactive elements are also leached out of FA if treated with H<sub>2</sub>SO<sub>4</sub> – 87% and 86% recovery rates were obtained for U and Th (Yermagambet et al., 2018).

Studies evaluating “co-extraction” of V and other elements during the H<sub>2</sub>SO<sub>4</sub> leaching of ashes/slags are rather scarce. Nevertheless, H<sub>2</sub>SO<sub>4</sub> is commonly used for the extraction of other elements in studies not including V (Table 6), such as Fe (Seidel and Zimmels, 1998), Al (Wei et al., 2018; Seidel and Zimmels, 1998; Valeev et al., 2022; Matjie and Bunt, 2005), As (Kashiwakura et al., 2010; Bradlo et al., 2015), Se (Kashiwakura et al., 2011), Y and Mn (Bradlo et al., 2015) or REE (Kashiwakura et al., 2013; Peiravi et al., 2017; Perämäki, 2014), as is shown in Table 6.

Even if in the aforementioned studies V was not evaluated, as the conditions are quite similar to those used for V leaching (Table 5), it can be expected that major proportion of V has been dissolved in these studies as well. On the one hand, it is advantageous if within one extraction step (using one leachant) multiple valuable elements are dissolved; on the other hand, low selectivity during the leaching makes higher demands on further processing of the leachate during the separation of the individual elements.

Since amorphous Al-bearing phase and Si-Al glass in coal ash are common host of V (and other trace elements) (Yang et al., 2020; Font et al., 2007), procedures improving Al leachability were tested also for the dissolution of V (and other trace elements) (Yang et al., 2020). However, even if thermal treatment of coal ash (originated from the combustion at 900 °C) with (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> at 400 °C (1 h) enhanced the Al solubility, the mobility of V (related to ash without (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> treatment) was significantly lower due to V co-precipitation with other ions. Namely at the temperatures higher than 60 °C, the formation of Fe- and Ti-bearing hydrate resulted in a significant decrease in V leaching efficiency (Yang et al., 2020). However, such coprecipitated V (and also Ga) ions can be quite easily re-dissolved by 0.1 M H<sub>2</sub>SO<sub>4</sub> (Yang et al., 2020; Font et al., 2007). Then, the dissolved V was higher than in case of coal ash without (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> treatment (Yang et al., 2020; Font et al., 2007).

#### 6.3.2. Leaching by diluted HCl

Dissolution of V in diluted HCl is generally lower than that in diluted H<sub>2</sub>SO<sub>4</sub>; nevertheless, 6% HCl (95 °C, 1 h) dissolved ca. 60–70% V from 3 coal ashes prepared in laboratory at 550–1100 °C (Wang et al., 2004). It was shown that Ni, Co, Cr, and Mn can be dissolved as well, but mobilities of namely Ni and Co were strongly dependent on ashing temperature with maximum dissolution observed after ashing at ca. 550 °C (and declining with increasing ashing temperature up to 1100 °C). Similar behaviour was also observed for Cr (or Mn) but to a lesser extent. At ca. 850 °C (simulating FBC), mobilities of Ni, Co, and Cr were ca. 50%, leachabilities of Mn were higher (ca. 80%) and not so temperature

**Table 6**  
Results of studies on H<sub>2</sub>SO<sub>4</sub> leaching of FAs not including V.

| Sample                       | Procedure   | Leached   | Ref.                       |
|------------------------------|---|---|----------------------------|
| High-Al coal FA              | H <sub>2</sub> SO <sub>4</sub> :FA = 1.2<br>Conc. H <sub>2</sub> SO <sub>4</sub><br>t > 230 °C<br>100 min                               | 86% alumina   | (Wei et al., 2018)         |
| Coal FA                      | Dilute H <sub>2</sub> SO <sub>4</sub> (1 or 0.1 M)<br>10 min<br>100 g FA – 1 L H <sub>2</sub> SO <sub>4</sub><br>Laboratory temperature | Rapid dissolution of As, decrease in solubility with increasing pH  | (Kashiwakura et al., 2010) |
| ESP FA (bitum. coal+biomass) | pH 1–13<br>(H <sub>2</sub> SO <sub>4</sub> -NaOH)   | At pH = 1, high dissolution of elements forming oxygen anions (As, Cr, B, Mo, Sb, Se, V, and W)             | (Bradlo et al., 2015)      |
| Coal FA                      | 5 g FA: 500 mL H <sub>2</sub> SO <sub>4</sub> , 30–80 °C, 2 h   | 45% dissolution rate of La, similar behaviour for Ce, Sc, Y, Pr, Nd, Sm, Gd, Eu, Tb, Dy, Ho, Er, Tu, Yb, Lu | (Kashiwakura et al., 2013) |
| Coal ash                     | H <sub>2</sub> SO <sub>4</sub> , 30–80 °C, 2 h  | 8–45% REE   | (Peiravi et al., 2017)     |
| Coal FA                      | 100 g FA – 1 L H <sub>2</sub> SO <sub>4</sub> (0.1 or 1 M),<br>25 °C, 600 s   | Rapid dissolution of Se, decrease in solubility with increasing pH  | (Kashiwakura et al., 2011) |
| Industrial FA                | 0.4 M H <sub>2</sub> SO <sub>4</sub><br>Ultrasonic bath after oxalic acid pre-treatment<br>18 min                                       | 70% of the REE  | (Perämäki, 2014)           |

dependent. These values (related to ashes from 3 different coals) are mutually similar and might have been used as rough estimation of behaviour of FBC ash in terms of the temperature; nevertheless, during FBC huge amount of calcareous additives are typically used, which could affect V leaching behaviour due to formation of Ca-V compounds (Nugteren et al., 2002; Izquierdo and Querol, 2012). Industrial coal FA was leached by cold diluted HCl (0.5 M) as well providing 63% V recovery during 24 h and 67% after 7 days (Harris and Silberman, 1983).

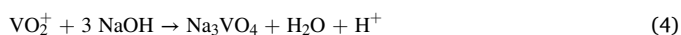
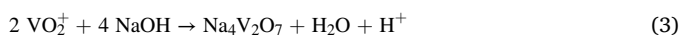
Other studies using HCl do not include V. Using 1 M HCl (85 °C, 4 h) ca. 80–90% REE was dissolved from PCC FAs (Middleton et al., 2020) or using cold HCl (HCl: H<sub>2</sub>O = 2:1, vol/vol) about 50% of Y was dissolved out of FBC FAs (Bartoňová et al., 2018). Dilute HCl was also tested for Ga recovery from coal FA – Fang and Gesser (1996) used 2 M HCl (24 h, ambient temperature) while Gutierrez (1997) used 6 M HCl (1 h, boiling point). Hence, in case of diluted HCl (temperature up to ca. 95 °C), V could be partially leached along with other elements, such as Ni, Co, Cr, Mn, Y, or REE. Compared to H<sub>2</sub>SO<sub>4</sub>, extraction yields are generally lower, but it can be used at least as an efficient “cleaning application” facilitating further use of the leached residues.

#### 6.4. Alkaline leaching/roasting

Literature on alkaline leaching of coal combustion wastes and related V data are rather scarce. Using weak base as a leaching agent (0.5 M NH<sub>4</sub>OH) dissolved during 24 h 29 ppm out of total 260 ppm V in coal FA, which is ca. 11% (Harris and Silberman, 1983). Font et al. (2007) reported < 64% V extraction yields from coal IGCC FA when using extreme alkaline extraction conditions (the recovery of Ga was much better – 98.8%).

##### 6.4.1. Comparison of H<sub>2</sub>SO<sub>4</sub> and NaOH leaching

Efficiency of alkaline and acidic leaching of V in ashes from soft asphalt fuels (15% V) was compared by Chmielewski et al. (1997) rejecting acid leaching as ineffective. Using alkaline leaching by 30% NaOH (2 h, 100–110 °C), the leaching efficiency of V was 94% and can be described by Eqs. (3) and (4) (Chmielewski et al., 1997):



After oxidation of V(4+) to V(5+) by 30% H<sub>2</sub>O<sub>2</sub>, neutralization of alkaline leachate to ca. pH= 8 by H<sub>2</sub>SO<sub>4</sub> and adding ammonium sulphate (or chloride), ammonium metavanadate precipitate is formed (Eq. (5)) (Chmielewski et al., 1997):

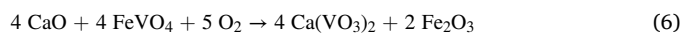


Navarro et al. (2007) compared 0.5 M H<sub>2</sub>SO<sub>4</sub> and 2 M NaOH leaching of oil FA (1.6% V) followed by the second step of V recovery from leachates by solvent extraction and selective precipitation. Both procedures led to ca. 98% recovery; however, using 2 M NaOH required more leaching repetitions (extraction steps). Despite this, alkaline leaching was evaluated to be better due to its selectivity for V (vs. other transition metals). Precipitation was preferred to amine extraction due to better selectivity as well.

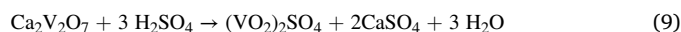
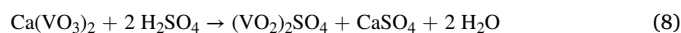
Comparison of acid and alkaline leaching of dumped FA from crude oil power plant by 0–5 M NaOH and 0–5 M H<sub>2</sub>SO<sub>4</sub> (96 h) exhibited comparable results (being for H<sub>2</sub>SO<sub>4</sub> slightly better). Both leaching agents were also evaluated in terms of the second step that followed – V retention from leachate on chitosan or V extraction with amine extractants – for both these procedures, acidic solution was evaluated as more advantageous. Therefore, extraction by H<sub>2</sub>SO<sub>4</sub> was recommended for this purpose (Guibal et al., 2003).

##### 6.4.2. Alkaline roasting – leaching method

If V occurs in the form of V-bearing spinels (Fe,Mg,Mn)<sub>x</sub>(V,Cr)<sub>3-x</sub>O<sub>4</sub>, alkaline roasting typically used for V slags may be efficient procedure (Li et al., 2016, 2015). As roasting with some sodium salts often generates corrosion gases (HCl, Cl<sub>2</sub> etc.), calcification roasting may be a cleaner procedure converting V-bearing spinels by CaO or CaCO<sub>3</sub> to Ca-vanadates, according to Eqs. (6) and (7) (Li et al., 2016):



Which is followed by H<sub>2</sub>SO<sub>4</sub> leaching (Eqs. (8) and (9)) (Li et al., 2016):



V retention in the aforementioned experiments were 96% and 98.9%, which documents efficiency of this approach.

#### 6.5. Bioleaching

Not only chemical leaching but also biotechnological approaches of metal recovery from waste materials have been tested. This approach is based on microbial activities converting insoluble metal compounds into water-leachable species. Advantages of bacterial leaching over the other methods are lower cost, using normal conditions, low energy

requirements and small areas for installation. Disadvantages are low growth rate of bacteria, low biooxidation rates and low selectivity (Snegirev and Sabirova, 2021; Park and Liang, 2019; Meer and Nazir, 2018).

Particular attention has been paid to using *autotrophic bacteria* (i.e. bacteria that do not require carbon substrate and use energy from oxidation of S-, Fe- or N-species) (Snegirev and Sabirova, 2021; Park and Liang, 2019; Meer and Nazir, 2018). In case of sulphidic materials, the most common is using chemolithotrophic bacteria, such as *Acidithiobacillus* sp. that convert metal sulphides into metal sulphates generating  $H_2SO_4$  (acidolysis) (Lee and Pandey, 2012; Brombacher et al., 1997). In case of non-sulphidic materials (minerals, wastes etc.), *heterotrophic microorganisms* (which require a substrate with organic carbon) are widely used. As a product of the metabolism of this substrate, such microorganisms produce acidic compounds, e.g. acetic, citric, oxalic or gluconic acids, able to dissolve oxides, silicates, carbonates, hydroxides etc. by reduction acidolysis and/or complexation (Jain and Sharma, 2004). Heterotrophic microorganisms used for bioleaching include bacteria (*Bacillus pseudomonas* etc.) (Jain and Sharma, 2004) or fungi (*Aspergillus*, *Penicillium* etc.) (Jain and Sharma, 2004; Lee and Pandey, 2012). Heterotrophic bacteria and fungi can tolerate high pH (Mirazimi et al., 2015).

Traditionally, if bioleaching was applied on coal combustion ashes/slugs, it was mostly conducted with the aim to extract Al by *Aspergillus niger* (Singer et al., 1982; Torma and Singh, 1993) or *Thiobacillus thiooxidans* (Fass et al., 1994; Seidel and Zimmels, 1998), Fe by *Thiobacillus thiooxidans* (Seidel and Zimmels, 1998) or Ti by *Rhodococcus* sp (Shabtai et al., 1993). Results related to V bioleaching from coal ashes /slugs are quite scarce, so some other wastes are mentioned herein as well. Bosecker (1987) concluded that if *Thiobacillus thiooxidans* was applied on 6 MSWI FAs, the V extraction recovery during bacterial leaching was as effective as in case of chemical leaching using  $H_2SO_4$  (in case of 4 samples out of 6, the mobilities were almost 100%). In case of LD converter slag with 1.97%  $V_2O_5$ , Mirazimi et al. (2015) observed better V removal by bacteria (ca. 80%) than by fungi (ca. 70%). In this study autotrophic (*Acidithiobacillus thiooxidans*) and heterotrophic (*Pseudomonas putida*) bacteria and heterotrophic fungi (*Aspergillus niger*) were used. Rastegar et al. (2015) achieved 82% V mobility by *Acidithiobacillus ferrooxidans* if applied on V-rich oil-fired ash with 49 g/kg V. Moreover, this procedure also mobilized 86% Ni and 87% Cu. A novel strain (*Bacillus mucilaginosus*) was tested for the V extraction from low-grade stone coal. The results from direct bioleaching with 57% recovery was significantly improved by the calcination of the stone coal prior to bioleaching achieving 85% V mobility (Dong et al., 2020).

Recently, promising results of V bioleaching from coal ash/slag have appeared.

Chronologically, Jadhav and Hocheng (2015) extracted V from pre-washed thermal power plant FA by citric acid producing *Aspergillus niger* 34770 Culture (30 °C, 4 h, S/L=1 g/100 mL) with extraction recovery of ca. 100%. During the same procedure, almost 100% recovery was obtained also for Cd, Co, Se, Ca, Cu, Mn, Fe, Al, Zn, Ti, B, K, and Mg, while in case of Cr, Ni, As, and Pb, it was slightly lower (93%, 83%, 78% and 70%, respectively). After the bioleaching, the seed germination, the root and shoot growth of *V. radiata* was substantially improved (in comparison with the original unleached FA).

Gluconic acid producing *Acidomonas methanolica* used by Kermer et al. (2017) for mobilization of elements from stabilized lignite ash provided 50–80% extraction not only for V, but also for Ce, Sr, Ti, and Zr.

Park and Liang (2019) compared bioleaching of V from coal FA (104 ppm V) by 3 microbial strains: *Candida bombicola*, *Phanerochaete chrysosporium* and *Cryptococcus curvatus* with extraction efficiency being 70.2%, 65.2% and 61.7%. In this study, ca. 30 elements have been evaluated and only As and Mo (and perhaps Sb) provided higher extraction recovery (> 60%) by *Phanerochaete chrysosporium* and *Cryptococcus Curvatus*. Using *Candida bombicola*, > 60% V, As, Mo, Sb, U, Sc,

Y, Dy, Er, and Yb has been leached.

The results indicate that the bioleaching efficiency is comparable to that of traditional chemical methods. For example, heterotrophic microorganisms produce organic acids (acetic, citric, oxalic, gluconic etc.) and metal complexation is common mechanism related to metal dissolution (Jain and Sharma, 2004). Using synthetic solutions of 0.01 M chelating agents for V dissolution from (260 ppm) coal ESP FA revealed 41% V dissolved by EDTA and 44% dissolved in citric acid after 7-day treatment (V recovery when using histidine or glycine was quite low - < 2%) (Harris and Silberman, 1983).

Latest papers document modern promising trends but unfortunately it does not include V data. A sequential integration approach of hydrothermal alkali treatment and bioleaching was applied to coal FA providing maximum leaching rates for Ti, Ga, Sr, Zr, Ba, and Bi being 97.6%, 71.4%, 72.4%, 87.0%, 45.6%, and 60.9%, respectively (Su et al., 2020).

## 7. Concluding remarks and future research perspectives

The study reviews crucial aspects related to V present in coal and corresponding ash and slag residues with particular attention paid to its potential extraction. The paper evaluates the results from traditional coal combustion as well as from modern technologies with great environmental benefits, such as co-combustion of coal and wastes or oxy-fuel combustion. The research areas evaluated in this study are:

- i) V levels in input materials - coal, wastes, or combustion additives (including speciation and modes of occurrence)
- ii) Thermodynamic equilibrium calculations of V behaviour during the combustion
- iii) V levels in corresponding ash and slag counterparts (and distribution among bottom ash/slag and fly ash, particulate control device rows and V speciation)
- iv) Physical separation methods - particle-size separation, magnetic separation, density separation, electrostatic separation etc.
- v) Chemical extraction procedures – leaching by water, various acids, or alkaline solutions including the effect of pH and roasting
- vi) Bioleaching and the comparison with traditional chemical dissolution

Average V concentrations in brown-coals and hard-coal are below 50 ppm, in brown-coal and hard-coal ashes the average levels are 100–200 ppm. If coal is co-combusted with other materials, V content in ashes/slugs can be lower (e.g., in case of agricultural or forest residues) or substantially higher (namely in case of petcoke). Using desulphurization additives generally results in a “diluting” effect on V in ashes due to low V levels in most calcareous additives. Regarding the selection of optimal material serving as a source of V, high V concentrations are in residues from co-combustion of coal and petcoke. From conventional combustion residues, FAs contain typically more V than bottom ashes/slugs; FAs from the last sections (hoppers) of ESP generally contain more V than the FAs from the first and second sections but relative abundance of FAs from the last rows is quite low. Coal ashes are mostly better V source than original coals; at least in the case that the combustion temperature is not too high. Hence, if fuel is energetically used, due to quite low V volatility its fraction in the form of gaseous emissions is low (a few %) and as a result of the thermal treatment V concentrations as well as its leachability is elevated (related to original coal).

Numerous *physical separation methods* have been tested to elevate V concentrations in ashes/slugs, such as particle-size fractionation, magnetic separation, density (sink-float) separation, electrostatic separation etc. None of these techniques generally cannot provide material with sufficiently high V concentration. Nevertheless, they can be used as pre-concentration procedures providing fractions with increased V content (toxicity of fractions depleted in V and other toxic elements is thereby reduced facilitating their handling, utilization or meeting the threshold

limits).

Hence, if production of V is the main objective, chemical or biological approach should generally follow the physical-separation pretreatment. Effective V extraction (leaching) procedures exist that mostly achieve > 90–95% V extraction yield. The residual amount of V (a few %) left after the extraction in the ash should not pose a problem in terms of toxic V-containing leachate as it is expected to be firmly bound in the leached ash/slag residue.

Despite high leaching efficiency, *chemical extraction of V* from conventional ash and slag wastes is not expected to be economically attractive. Therefore, an effort paid to incorporation of V recovery into more complex extraction scheme (providing more valuable components) seems to be more promising way how to economically obtain V from common combustion wastes. For example, good V extraction yields have been reported using H<sub>2</sub>SO<sub>4</sub>. Individual optimization of the extraction procedure facilitates achieving good V extraction results if applied on various materials – on conventional coal ashes/slugs, biomass ash, stone coal, asphaltite ash, heavy oil FAs or orimulsion FA. But only a few studies evaluate “co-extraction” of V and other elements by H<sub>2</sub>SO<sub>4</sub>, such as V and Y, V and Ni or V, Ce and Ge. Nevertheless, as H<sub>2</sub>SO<sub>4</sub> is widely used for the extraction of various other elements (than V), such as Al, As, Se, Y, and Mn or REE, due to similarity of conditions it can be expected that major fraction of V has been dissolved in these studies as well. However, dissolution of multiple elements from FA by the same leachant makes higher demands on further processing of the leached solution during the separation of the individual elements.

*V bioleaching studies* are even more scarce. A few papers appeared recently document that bioleaching is another promising approach showing that not only V but also other elements could be removed from coal ash. Nevertheless, only a few microbial strains have been tested for this purpose – *Aspergillus niger*, *Acidomonas methanolica*, *Candida bombicola*, *Phanerochaete chrysosporium* and *Cryptococcus curvatus*. Latest research documents that efficiency of bioleaching by *Aspergillus niger* from coal FA can be substantially increased by hydrothermal alkali pretreatment step, but this study does not evaluate V (it was focused to Ti, Ga, Sr, Zr, Ba, and Bi). Almost complete removal of V, Cd, Co, Se, Ca, Cu, Mn, Fe, Al, Zn, Ti, B, K, and Mg from FA was described in literature thereby effectively reducing strong harmful effect of untreated FA on seed germination, the root and shoot growth of *V. radiata* by *Aspergillus niger* bioleaching. Hence, the “cleaned” ash with reduced toxicity is another valuable benefit.

Therefore, overall, more valuable components could be extracted out of the ash/slag at the same time (such as V, Y, Sc, Ga, REE, etc.); moreover, the “cleaned” ash/slag residues with reduced toxicity and enhanced utilization perspectives should provide other benefits (reduced cost of landfilling, economic benefit from replacement of natural resources used e.g. in civil engineering, solving the supply risk of other critical materials etc.). Thus, techno-economic studies including such overall evaluation conducted with respect to all these aspects and benefits would be undoubtedly useful.

Hitherto the research in this area was focused predominantly to conventional coal combustion residues (ashes/slugs etc.). As power production is one of a major CO<sub>2</sub>-emitting sector, there is an intensive decarbonization effort leading to a rapid development of modern technologies mitigating CO<sub>2</sub> emissions, such as oxy-fuel combustion, IGCC (combined optimally with CO<sub>2</sub> capture), co-firing with low C or C-neutral fuels or carbon capture technologies. Hence it can be expected that new industrial wastes will be generated in near future in vast quantities, which is also worth research attention as the literature in this field is currently rather limited.

#### CRediT authorship contribution statement

**Lucie Bartoňová:** Conceptualization, Writing – original draft, Writing – review & editing. **Helena Raclavská:** Writing – original draft, Writing – review & editing, Supervision. **Jan Najser:** Writing – original

draft.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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