Microstructural and chemical characterization of stabilized spent vanadium pentoxide catalyst in copper smelting slag

F Coronado, A Valenzuela Soto, M A Encinas Romero, O Hernández-Negrete \(^1\) and G Tiburcio Munive \(^1\)

Department of Chemical Engineering and Metallurgy, University of Sonora, Hermosillo, Mexico

\(^1\) Authors to whom any correspondence should be addressed.

E-mail: ofelia.hernandez@unison.mx and guillermo.munive@unison.mx

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1. Introduction

Unsustainable economic activities generate a wide range of pollutants that have negatively impacted the environment \([1–3]\). Some of these pollutants are toxic compounds that have severe effects on the health of living beings \([1, 2]\). Further, it has been proved that they affect the ecological balance of the environment, threatening plants, animals, and the human population \([1–3]\). In particular, the extractive metallurgical processes that are involved in the mining activities generate large amounts of toxic waste composed of minerals and significant amounts of slag \([1–4]\). Without proper handling and disposal, this waste is potentially dangerous to the environment due to its toxicity \([1–3]\).

For the reasons stated above, the mining industry is interested in developing disposal techniques to prevent the contamination of landfills and water effluents. By doing so, the mining industry shows its compromise with the environment and prevents environmental liabilities \([5]\). For example, the high toxicity of vanadium pentoxide \((V_2O_5)\) used as a catalyst to produce sulfuric acid \((H_2SO_4)\) in the copper mines demands actions to prevent contamination of soils and water sources \([3, 5]\).

The research on the biological role of vanadium and some vanadium compounds is gaining importance in recent years due to its well-known toxic, mutagenic and genotoxic potential in a wide variety of biological systems, and particularly vanadium pentoxide has been classified by the IARC (2006) as a possible carcinogen for humans \([6]\).

The copper smelting slag (CSS) is a waste material obtained from the process of copper refining, which is carried out through pyrometallurgical processes of copper sulfide minerals, after their concentration through the flotation process. During the fusion of the material (concentrate), two separable or immiscible liquid phases are produced: copper-rich matte and copper smelting slag. The matte, according to its copper content, then passes to the refining process while the molten slag is discarded directly or goes to the copper recovery process.

The CSS consists of oxides contained in the furnace charge and the iron oxides that are produced by oxidation during pyrometallurgical processing of copper. Its composition depends on the nature of the ore, the
concentrates, gas flows, the operating conditions, and various other factors. The oxides present are FeO, Fe₃O₄, SiO₂, and Al₂O₃, to mention the most important.

Specifically, the slag from the Mexican copper smelter, which is the one used in this study, has the following components: FeO, SiO₂, Al₂O₃, SO₃, ZnO, K₂O, CuO from the most predominant.

Pyrometallurgical processing is widely used for metals refining [4]. This technique uses heat to produce physical and chemical transformations in the used raw materials to produce recoverable materials. One of the most typical modes of this technique is smelting, where the raw materials are heated to melted and form stable components during solidification.

This study aims, the stabilization of the V₂O₅ present in the SVC by pyrometallurgical processing (smelting experiments) of both waste materials; the spent V₂O₅ catalyst along with copper smelting slag. The chemical and microstructural characterization of the fused compound obtained by the smelting of the two waste materials from the copper mining industry. To recognize if the stabilization methodology proposed would form compounds that are naturally stable under atmospheric conditions.

2. Experimental details

2.1. Sample preparation for characterization techniques

Raw samples of pellets of spent V₂O₅ catalyst (SVC) and Copper Smelting Slag (CSS) were characterized throughout SEM-EDS, XRD, and DTA-TGA. The SEM-EDS characterization of the SVC samples was longitudinally and transversally due to their geometry. SVC and CSS samples were crushed and ground to −100 mesh for XRD and DTA-TGA experiments. CSS bulk samples were prepared by conventional metallographic preparation for microstructural characterization, and this involved cold mounting in resin, grinding with SiC paper (from 240–2000 grit), and cloth polishing with alumina suspension from 6–1 μm for surface finish.

2.2. Preparation of fused compounds (FC)

The stabilization process starts with the preparation of the starting materials for the experiments. The SVC pellets and CSS lumps were crushed and ground to get powders of particle sizes of −100 mesh to improve surface area contact. Fused compounds were obtained by fusion experiments with catalyst/slack 1:4 ratio performed by placing 90 g of slag in both SiC and Al₂O₃ crucibles to melt at 1250 °C for 20 min. After the melting of the CSS, the crucibles were removed from the furnace and added 20 g of the SVC along with 10 g of CSS on the top to prevent the V₂O₅ evaporation. The crucibles were placed back in the furnace for melting to about 30 min, and after this time, these were removed from the furnace to be air-cooled to room temperature. The specimens were weighed and crushed and grounded to −100 mesh for characterization. It was observed that SiC crucibles reacted with the fused compound; thus, the samples prepared in this crucible were discarded.

2.3. Characterization

The characterization of CSS, SVC, and FC samples was performed in a scanning electron microscopy with an X-ray dispersive energy analyzer (SEM / EDS). Observation of the materials by using an SEM Jeol JSM 5410 LV in the backscattered electron (BSE) mode and microanalysis via energy-dispersive X-ray spectroscopy (EDS). EDS standards were performed with the use of high purity specimens of Fe, Si, V, Cu, Ti, Zn, and As standards that were polished to 1 μm finish. At least five large-area analyses were performed in samples, and at least ten analyses were obtained from each phase (spot analyses) with a minimum size of 5 μm for local compositions.

Powder samples were used for phase characterization in a Bruker Advance D8 X-ray diffractometer with CuKα radiation (λ = 1.54174 Å), in a 20 interval from 10° to 80° and a step size of 0.02°. The experimental XRD diffractograms were analyzed using the JCPDS (International Centre for Diffraction Data) database through Match!1.10 Software interface. From the analysis, we selected those phases with the best fit compared to our data.

Simultaneous DTA/TGA experiments were performed in the SDT 2960 thermal analyser from room temperature to 600 °C and 1400 °C using airflow of 50 cm³ min⁻¹ at a heating rate of 10 °C min⁻¹.

3. Results

3.1. Copper smelting slag and spent V₂O₅ catalyst characterization

The backscattered electron (BSE) images in figure 1 show the typical microstructure of the copper smelting slag CSS. The microstructure of the CSS is a Fe and Si-rich matrix (table s.1 is available online at stacks.iop.org/MRX/7/016521/mediala) with a considerable volume fraction of copper-rich bright particles (figure 1(a)). According to EDS chemical analyses, the CSS was mainly composed of Fe and Si with other elements as minor
components (table s.1). The chemical analyses taken for this research correspond to the average of at least five analyses in different areas. The figure 1(b) and table s.3 shows, the analyzed areas in the CSS, with bright contrast that presented a range of particle sizes from 5–100 μm. The microstructure also presented faceted grains with light grey contrast that were both isolated and surrounding the bright copper-rich grains; their sizes ranged from 5–80 μm (figure 1(a)). The chemical compositions in table s.3 correspond to the labeled regions in figure 1(b). The chemical analysis taken in the light grey areas labelled with D and A in figure 1(b) showed that these grains presented high Fe and Si contents and that A also shows more volume fraction of black phase presented a higher Si content and lower Fe content than D. The analysis performed in the C areas (figure 1(b)) showed the higher content of Cu.

The measured elements depicted in table s.1 are present in the compounds shown in table s.2. According to the balance of the data from table s.1, the CSS is mainly composed of 2FeO.SiO2 (Fe2SiO4 Fayalite) as mayor component with some Al2O3, ZnO, K2O and Cu, and CuO as minor components (table s.2), which are consistent with the data in figure 2.

According to the results obtained from XRD analysis performed in bulk, it was found that the CSS was composed of Fe2SiO4 (JCPDS card 71–1669), CuO (JCPDS card 80–1917), SO3 (JCPDS card 72–1664), Fe3O4 (JCPDS card 72–2303) corresponding to the best fit of the peaks in the XRD experimental diffractogram (figure 2). EDS analysis also detected other minor components which could be under the detection limit for the XRD analysis (table s.1).

3.2. Spent V2O5 catalyst (SVC) characterization

The image of the typical surface microstructure of the SVC pellets is shown in figure 3(a). This image shows the morphology of the powdery surface of the SVC pellets. Chemical analyses depicted in table s.4 showed that the pellets are rich in Si, and this is because the catalyst is SiO2 supported. EDS chemical analyses shown in table s.6,
suggest local compositions effects in the SVC; the bright A regions in figure 3(b) corresponded to vanadium and arsenic-rich areas, while B areas with darker contrast presented higher contents of Si, S, K and Al and scarcity of vanadium. Thus, the surface of the SVC did not present a homogeneous distribution of V2O5 consistent with the typically spent catalyst. Chemical analyses were performed both in longitudinal and cross-section areas of the SVC pellets, and the results were similar. Arsenic content in the pellets was because of the poisoning with arsenic during processing.

According to XRD analysis the SVC was mainly composed of SiO2 (JCPDS card 43–596), V2O5 (JCPDS card 77–2418), V2O3 (JCPDS card 34–187), SO3 (JCPDS card 72–1664), As2O3 (JCPDS card 15–778), Al2O3 (JCPDS card 46–1212), and K2O (JCPDS card 23–493), which corresponded to the best fit of the peaks in the experimental diffractogram (figure 4). Other components with minor contents were also detected by EDS analysis, but their content was under the detection limit for the XRD analysis (table s.4).

The typical oxide composition of the SVC is enlisted in table s.5. According to EDS analyses in table s.5, the significant components are SiO2, SO3, K2O, and V2O5, while minor contents of Al2O3, Na2O, SO3 were also detected. All this data agrees well with the typical V2O5 catalyst supported in SiO2 [7, 8].

DTA-TGA plot of the SVC is shown in figure 5. The TGA curve presents three critical intervals of mass loss, while the DTA curve did not show any significant reactions upon sample heating up to 600 °C.

In the TGA curve, it is possible to observe a mass loss of 7.5% from room temperature to about 120 °C, and further sample heating shows an increase of mass from 92.5 to 94% up to 430 °C. And finally, a mass loss of 3.3% of mass to about 90.7 at 590 °C was observed, which could be associated with the evaporation reaction as a result of the decomposition of SO3 into SO2. The heating rate used for the DTA-TGA experiments was too slow to show significant reactions in the heating of the SVC sample.
3.2.1. Fusion tests

The images in figure 6 show the starting SVC and CSS (−100 mesh) powders used in the fusion test for the V2O5 stabilization. The SVC presented a finer granular microstructure (figure 6(a)) than that of the CSS in figure 6(b), which comprised of coarse granular particles with different contrasts under back scattered conditions. It is suggested that the SVC was very hygroscopic since the fine granular particles are found mostly linked; the presence of sulfuric acid and SiO2 contents are typically related to this effect.

3.3. Characterization of fused compound

The sample was a black lump that was crushed and grounded for analysis. The typical microstructure under the backscattered conditions of the fused compound is observed in figure 7. The contrast could indicate a homogeneous composition. The insert image in figure 7 shows a close view of the typical particles in the obtained fused compound.

According to EDS chemical analyses shown in table s.8, the sample of the fused compound presented vanadium in its composition. The vanadium content in the fused compound is consistent with the CSS/SVC ratio of 4:1, and its distribution in the fused compound was homogeneous. According to EDS chemical analyses in table s.8, Fe, Si, and O were the main elemental components in the fused compound.

According to XRD analysis, the fused compound comprised of the Fe2SiO4 phase (JCPDS card 71–1669) and Fe3VO4 phase (JCPDS card 29–736) corresponding to the best fit of the peaks in the experimental diffractogram (figure 8). EDS analysis also detected other minor components which could be under the detection limit for the XRD analysis (table s.8).
The DTA-TGA plot in figure 9, indicates the stability of this compound to about 650 °C, while there is no relevant reaction in the DTA curve at any temperature, which would indicate that the phases formed during fusion experiments are stable up to 1400 °C.

4. Discussion

According to XRD and EDS analysis from figures 1(b) and 2, and table s.1, the CSS was mainly composed of the Fe₂SiO₄ phase (2FeO·SiO₂), which are consistent with images in figure 1 where the Fe₂SiO₄ phase presented the higher volume fraction in the CSS microstructure. Thus, it is expected that the main reactions upon fusion would occur via the participation of this phase following the equation (1). In the FeO-SiO₂ diagram phase, the Fe₂SiO₄ phase melts congruently at 1205 °C, and it also forms under the eutectic reaction L → FeO + Fe₂SiO₄ at the eutectic composition of 23 molar % SiO₂ at 1183 °C. Besides, Fe₂SiO₄ also forms via the eutectic reaction L → Fe₂SiO₄ + SiO₂ at 1185 °C at 43 molar % of SiO₂ were it is found in equilibrium with SiO₂ (tridymite) [9].

\[
2\text{FeO}(s) + \text{SiO}_2(s) = \text{Fe}_2\text{SiO}_4(s)
\]

(1)

On the other hand, vanadium can form multiple oxides with different valence states, as can be seen in the V–O binary system. The SVC used for this research was mainly in the form of V₂O₅ in agreement with the XRD and the EDS chemical analyses (figure 4, tables s.4, s.5, and s.6). The latter is a stable compound under 1300 °C [10, 11]. The V₂O₃ suffers a thermal decomposition to V₂O₅ at high temperature, via VO were loss of oxygen occurs under low oxygen pressures [4, 10–12]. DTA-TGA plot of the SVC in figure 5 showed a mass loss related
to the evaporation of \( \text{H}_2\text{SO}_4 \) retained in the SVC while mass gain could be the result of some oxidation of the compounds in the SVC.

The following reaction depicts positive free Gibbs energies for a range of temperatures [13], which could indicate that the direct reaction of FeO and V\(_2\)O\(_5\) to produce the Iron vanadate FeVO\(_4\) is not possible.

\[
\text{FeO(s)} + \text{V}_2\text{O}_5(s) + \text{O}_2 = 4\text{FeVO}_4(s)
\]

However, the negative Gibbs energies calculated for the formation of the iron vanadate FeVO\(_4\) correlates with the FeO oxidation to form Fe\(_2\)O\(_3\), which is found to react with V\(_2\)O\(_5\) [14, 15] in the following route according to a thermodynamic study:

\[
2\text{FeO(s)} + \frac{1}{2}\text{O}_2(g) = \text{Fe}_2\text{O}_3(s)
\]

As the temperature raises, Fe\(_2\)O\(_3\) would quickly react with V\(_2\)O\(_5\) to form FeVO\(_4\) in the following manner:

\[
\text{Fe}_2\text{O}_3(s) + \text{V}_2\text{O}_5(s) = 2\text{FeVO}_4(s)
\]

This route is consistent with the final composition of the fused compound of this research. The main components were FeO, SiO\(_2\), and V\(_2\)O\(_5\) of the interest. According to [10] in the FeO–SiO\(_2–\)V\(_2\)O\(_5\) ternary system under isothermal conditions at 1300 and 1400 °C, the V\(_2\)O\(_5\) presented higher activity, and its activity depended very much on time.

In our experiments, the CSS was the first to melt at the set temperature of 1250 °C, and sulfur might be lost as evaporation, but Fayalite is liquid at this temperature (2FeO.SiO\(_2\)). The composition of the liquid CSS would be altered by the addition of the SVC (rich in SiO\(_2\), SO\(_3\), V\(_2\)O\(_5\), and more CSS on top of the liquid CSS).

The following reactions could have occurred upon the solidification of the obtained fused compound:

- The primary phase to solidify would be the Fe\(_2\)SiO\(_4\) (with melting point 1205 °C), following in the second place the reaction to form the iron vanadate FeVO\(_4\) (with melting point 850 °C) that could have formed as a result of the V\(_2\)O\(_5\) high chemical activity upon other minor components in the melt.
- The minor components could have remained in solid solutions of the present phases, but they were not detected by our XRD experiments. The BSE image in figure 7 did not show any considerable contrast to be able to identified the grains of the FeVO\(_4\) in the fused compound, which could indicate that this phase remained with a very fine microstructure.

Thus, the solidification of the fused compound could have occurred following the sequence of equations 1, and 4, which depicts two stable phases in equilibrium in atmospheric conditions.

Lixiviation experiments of the fused compound at different CSS/SVC ratios would be performed to test the chemical stability of the V\(_2\)O\(_5\) fixed in the FeVO\(_4\) + Fe\(_2\)SiO\(_4\) fused compound to evaluate if vanadium still can be dissolved after its disposal.

![Figure 9. DTA-TGA plot from fused compound.](image-url)
5. Conclusions

Based on the results obtained, the V₂O₅ contained in the SVC pellets was successfully fixed in the CSS by pyrometallurgical reactions that occurred during solidification of the SVC + CSS melt from 1250 °C.

The obtained fused compound consisted of Fe₂SiO₄ and FeVO₄ phases, which are found to be stable at atmospheric conditions.

The fused compound could be a viable option to safely discard the present mining waste materials and prevent further contamination of the toxic V₂O₅ compound into landfills and water effluent.

It is advisable to run lixiviation experiments to evaluate the dissolution of the components in the fused compound.

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ORCID iDs

O Hernández-Negrete 🥇 https://orcid.org/0000-0002-9875-9191

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