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METALLIC OXIDE MICROPHASES IN FLY ASHES: AN ULTRASTRUCTURAL INVESTIGATION

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Fly ashes from fuel oil combustion consist almost entirely of hollow, spheroidal formations, cenospheres, with sizes ranging from about 10 to 100 μm . These particles, produced during microdrop fuel oil combustion, look like droplet skeletons with numerous holes irregularly distributed on their surface.

Heavy metals are present in fly ashes mostly like crystalline sulphate or oxide phases located into the cenosphere hollow.

In this paper oxide phases were studied. They turned out to be prevalently composed of small particles with irregular shapes and sizes ranging from less than 0.1 μm to about 1 μm .

Oxide microparticles were classified by cluster analysis; the atomic percentages of eight metallic elements—Fe, Ni, V, Al, Cr, Mg, Zn, Ti, that represent virtually all the cations revealed in the composition of the oxides—were used to evaluate the "degree of similarity".

On the basis of the obtained chemical, compositional and morphological data the structure of the major metallic oxide phases was defined.

KEY WORDS: Fly ashes, metallic oxides, combustion processes, analytical transmission electron microscopy.

INTRODUCTION

Among the factors that are to be considered when evaluating the environmental impact of fly ashes from fuel oil combustion processes, there is the presence of heavy metals and the crystal-chemical characteristics of the phases to which these metals are bound—the leaching mechanisms through which metals are released in the environment being dependent on these characteristics¹.

Fly ashes consist almost entirely of hollow, spheroidal formations, the cenospheres. These particles are produced during microdrop fuel oil combustion when air and fuel are injected into the combustion chamber; they look like droplet skeletons (Figure 1) with numerous holes irregularly distributed on their surface.

The cenospheres have a wide granulometric spectrum with sizes ranging from a few to more than hundred microns. The composition and structure looks like essentially the same both for particles in micrometer range and for particles larger than 100 microns.²

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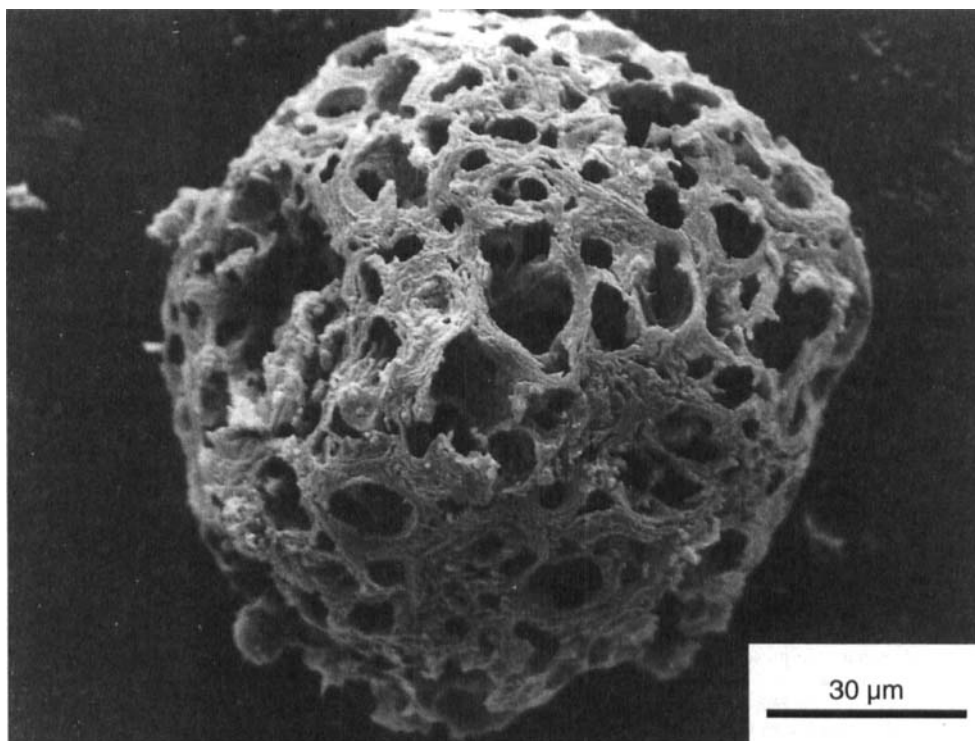


Figure 1 A typical cenosphere from a power plant burning fuel oil (SEM).

Recently, metals in fly ashes have been shown to be present mostly under the form of crystalline sulphate or oxide phases located into the cenosphere hollows².

The oxide phases turn out to be composed prevalently of binary oxides of V and Ni, V and Fe, Ni and Fe, with only minor contamination by different divalent (Zn, Mg) and trivalent (Cr, Al) cations². Quite reduced as well is the presence of oxide phases of only one kind of cation (for instance V, or Fe, or Ni).

The paper deals more in depth with the structure of metal oxide phases in cenospheres because of the importance that the leaching of heavy metals from ashes has from environmental and toxicological points of view.

EXPERIMENTAL

Oxide phase samples were obtained from cenospheres collected in the electrostatic precipitator of a power plant burning fuel oil.

Cenospheres were ground in an agate mill by a wet (isopropyl alcohol) grinding method to make their inner oxide phases available.

The cenosphere fragments were collected onto a cellulose nitrate filter on which a carbon film was evaporated; $3 \times 3 \text{ mm}^2$ square portions of the cellulose filter were mounted on a TEM Cu grid and exposed to acetone vapours until complete filter dissolution. Metal oxide phases were studied by analytical electron microscopy; a high voltage Philips TEM EM430 instrument equipped with an energy dispersion X-ray

spectrometer (EDXS) (EDAX 9900) and an electron energy loss spectrometer (EELS) (Gatan 607) were used.

RESULTS

Composition of the metal oxide phases

The composition of about 130 oxide phases was studied; the phases turned out to be constituted by small particles with irregular shapes and sizes ranging from less than $0.1 \mu\text{m}$ to about $1 \mu\text{m}$.

The atomic percentage of the different metallic elements in the oxide phases was estimated using a standardless x-ray microanalysis procedure and considering the "thin specimen" approximation, which is well based for our experimental conditions (electron beam energy 250 KeV, specimen thickness $\ll 1 \mu\text{m}$)³.

Oxide microparticles (Figure 2) were classified by cluster analysis; the atomic percentages of eight metallic elements—Fe, Ni, V, Al, Cr, Mg, Zn, Ti, that represent virtually all the cations revealed in the composition of the oxides—were used to evaluate the "degree of similarity" or, more exactly, the "distance" between two oxide particles in the "space of the metallic elements".

To measure this "distance" the Euclidean distance was used, i.e. $[\sum_i (x_i - y_i)^2]^{1/2}$, where x_i and y_i are the atomic concentrations of the "i" element in the x particle and in the y particle, respectively.

Clusters were constructed in such a way that the differences in particle composition were as small as possible within a cluster and as great as possible between clusters (minimising the intra-cluster distance variance and maximising the inter-cluster distance variance).

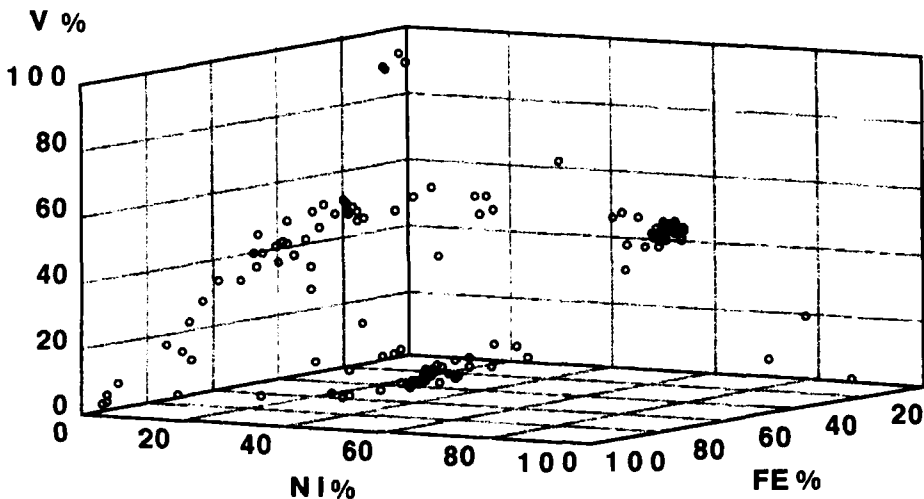


Figure 2 Distribution in the Fe-Ni-V "space" of 130 oxide microparticles from fly ashes (the atomic ratios are reported).

About 75% of the particles was classified in four clusters corresponding to:

- a) a Fe-Ni binary oxide phase (Figure 3)—in which the atomic ratio $\text{Fe/Ni} \approx 5/3$ —with crystalline habit and polyhedral morphology;
- b) a V-Ni binary oxide phase (Figure 4)—in which the atomic ratio $\text{Ni/V} \approx 5/4$ —with crystalline habit and lamellar morphology;
- c) a V-Fe binary oxide phase (Figure 5)—in which the atomic ratio $\text{V/Fe} \approx 5/3$ —with crystalline habit and not well defined morphology;
- d) a second V-Fe binary oxide phase—in which the atomic ratio V/Fe ranges from $\approx 4/5$ to $\approx 4/8$. This phase presents amorphous aggregates without a definite morphology.

The remaining 25% of the particles showed a more heterogeneous composition and were classifiable in a number of clusters composed of simple oxides—Fe oxide, 8% of the particles; V oxide, 3% of the particles; Ni oxide, 2% of the particles—or of oxide phases where Al, Ti, Fe were prevalent along with small atomic percentages of V and Ni.

To validate the cluster classification of the oxide particles, we verified whether the mean concentrations of the eight metallic elements detected in the particles were significantly different between clusters. Table 1 reports the mean metallic element concentrations, and Table 2, the p values obtained in a t -test series concerning the clusters defined above under a), b), c), d).

By comparing the two tables it was possible to verify that actually clusters a, b, c and d differ significantly (at $p < 0.05$) for more than 80% of their compositions with the exception of clusters a and d for which, nevertheless, the compositions differ significantly for about the 50%.

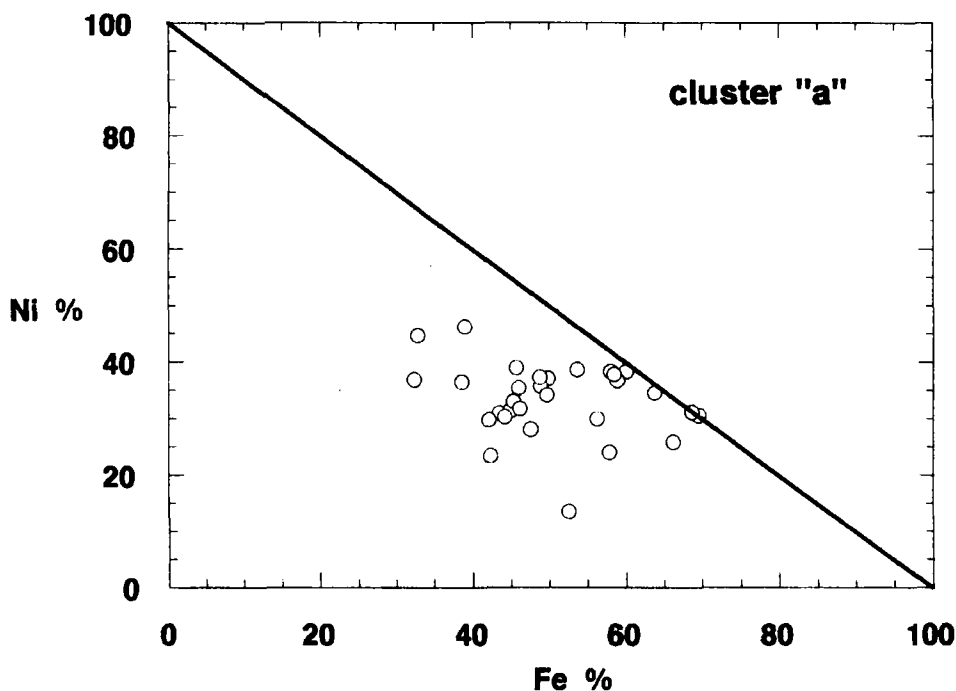


Figure 3 Distribution on the Fe-Ni plane of the oxide phases of the cluster "a" (the atomic ratios are reported).

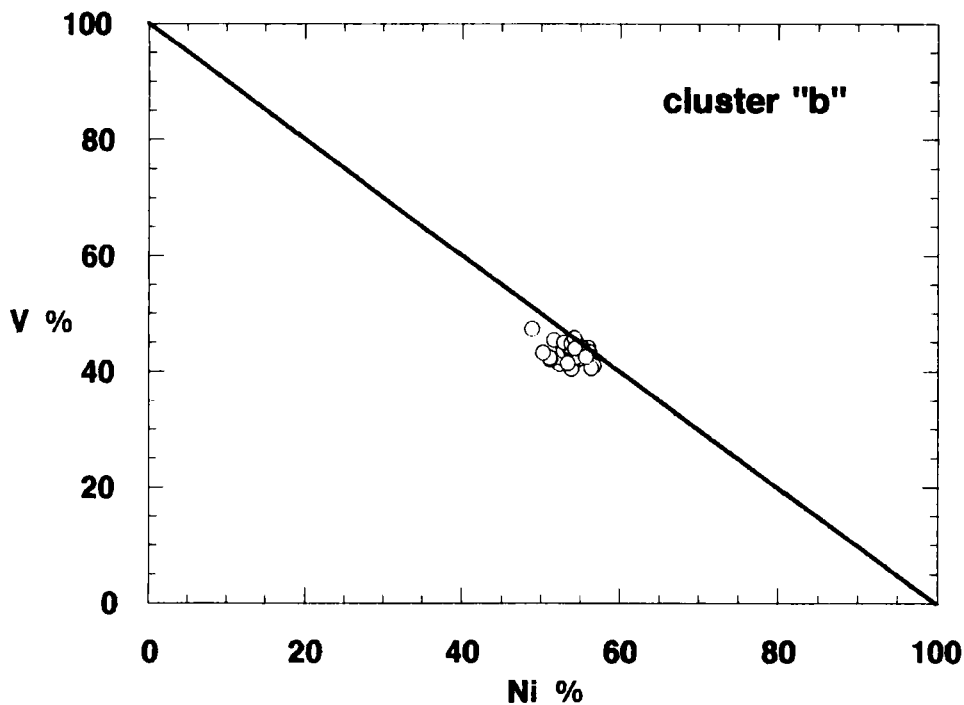


Figure 4 Distribution on the Ni-V plane of the oxide phases of the cluster "b" (the atomic ratios are reported).

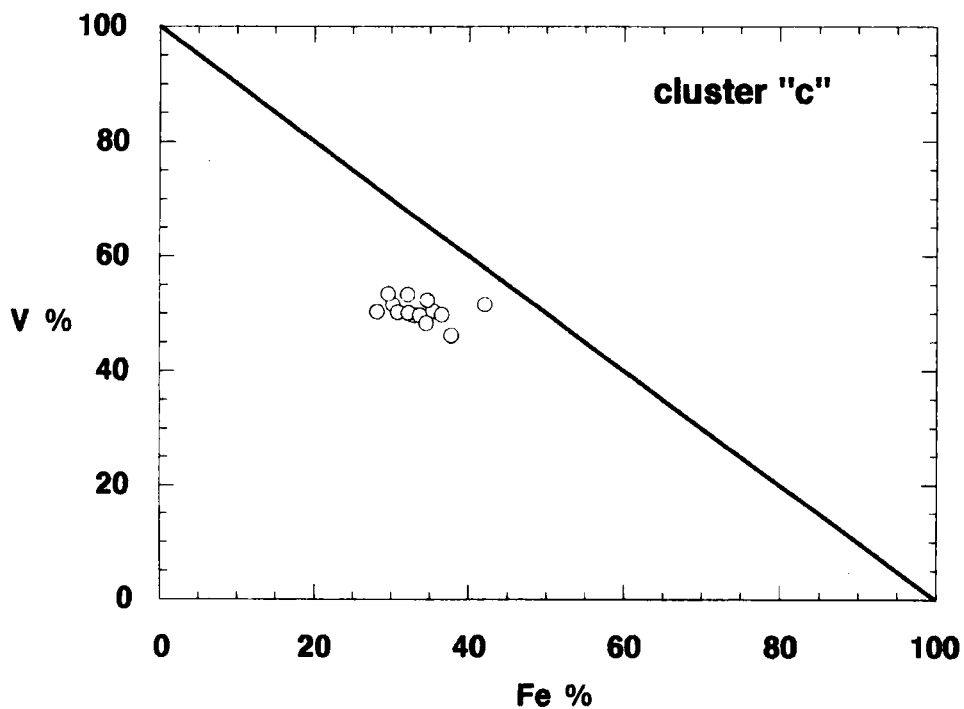


Figure 5 Distribution on the Fe-V plane of the oxide phases of the cluster "c" (the atomic ratios are reported).

Table 1 Atomic mean concentrations (%) of the metallic elements.

	<i>Cluster a</i>	<i>Cluster b</i>	<i>Cluster c</i>	<i>Cluster d</i>
Fe	50.3	1.6	33.6	48.3
Ni	33.4	53.7	8.3	4.4
V	3.8	43.3	50.5	39.9
Al	5.3	0.0	1.3	1.0
Cr	2.7	0.0	3.3	0.1
Mg	0.2	0.6	0.6	0.0
Zn	1.9	0.1	0.4	0.8
Ti	0.6	0.0	0.2	0.3

Table 2 T-test (2-tailed p).

	<i>For clusters a & b</i>	<i>For clusters a & c</i>	<i>For clusters a & d</i>
Fe	0.00000	0.00000	0.48308
Ni	0.00000	0.00000	0.00000
V	0.00000	0.00000	0.00000
Al	0.00001	0.02346	0.01171
Cr	0.00000	0.75207	0.16284
Mg	0.02638	0.20411	0.00000
Zn	0.01272	0.13251	0.29169
Ti	0.01170	0.27543	0.40704
	<i>For clusters b & c</i>	<i>For clusters b & d</i>	<i>For clusters c & d</i>
Fe	0.00000	0.00000	0.00000
Ni	0.00000	0.00000	0.00298
V	0.00000	0.00523	0.00000
Al	0.09281	0.00035	0.80241
Cr	0.00000	0.00000	0.00746
Mg	0.99148	0.00000	0.00000
Zn	0.05340	0.00012	0.15485
Ti	0.00648	0.00040	0.61829

Vanadium chemical state

To study the chemical state of V atoms in the V-Fe and V-Ni phases, Energy Loss Near Edge Structure (ELNES) measurements on the V-L_{2,3} edge, located at about 510 eV, were performed.

As it is well known⁴ both the edge location (in eV), and the near edge features (in the first 30 eV beyond the edge onset), contain useful information about the metal oxidation state and its bound symmetry.

Because of the difficulties in the theoretical interpretation of ELNES features we performed V-L_{2,3} edge measurements on reference samples prepared with commercial powders.

Specifically, we prepared standards of V₂O₃ (V³⁺), VO₂ (V⁴⁺), VC (V⁴⁺), V₂O₅ (V⁵⁺). The relative spectra are shown in Figure 6 together with the pure metal (V) spectrum.

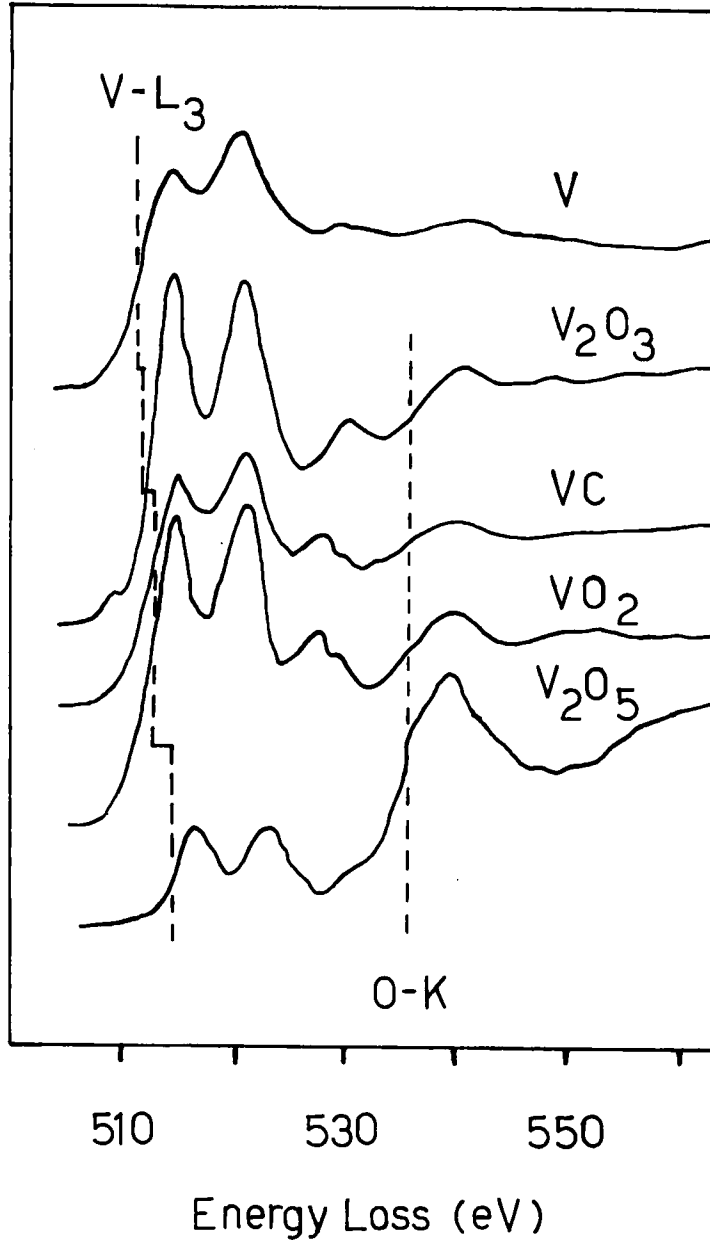


Figure 6 V- $L_{2,3}$ and O-K edges relative to pure metallic V, V_2O_3 , VO_2 and V_2O_5 standard samples.

As it can be noted a "chemical shift" in the V- $L_{2,3}$ edge onset occurs as from about 510 eV of the pure V, up to about 516 eV for the V_2O_5 (V^{3+}) spectrum. V_2O_3 (V^{3+}), VO_2 (V^{4+}) and VC (V^{4+}) show onsets located half way.

It is interesting to observe the evolution of the near edge features; in particular, the location of the third peak—before the O-K edge onset (at about 532 eV)—changes

dramatically from V_2O_3 (V^{3+}) to VO_2 (V^{4+}) or VC (V^{4+}). On the contrary, it remains virtually the same for VO_2 (V^{4+}) and VC (V^{4+}).

By following the edge onset and the third peak location, we are able to distinguish between V^{3+} , V^{4+} and V^{5+} .

Figure 7 reports the spectra relative to V-Ni and V-Fe. In the V-Ni spectrum the edge onset is located at about 513 eV and the third peak at about 528 eV, in agreement with the values of VO_2 (V^{4+}) and VC (V^{4+}). In the V-Fe spectrum the edge onset is located at about 516 eV and the third peak is not resolved because of the overlapping of the O-K edge. This important shift suggests a strong oxidation of V, i.e. V^{5+} .

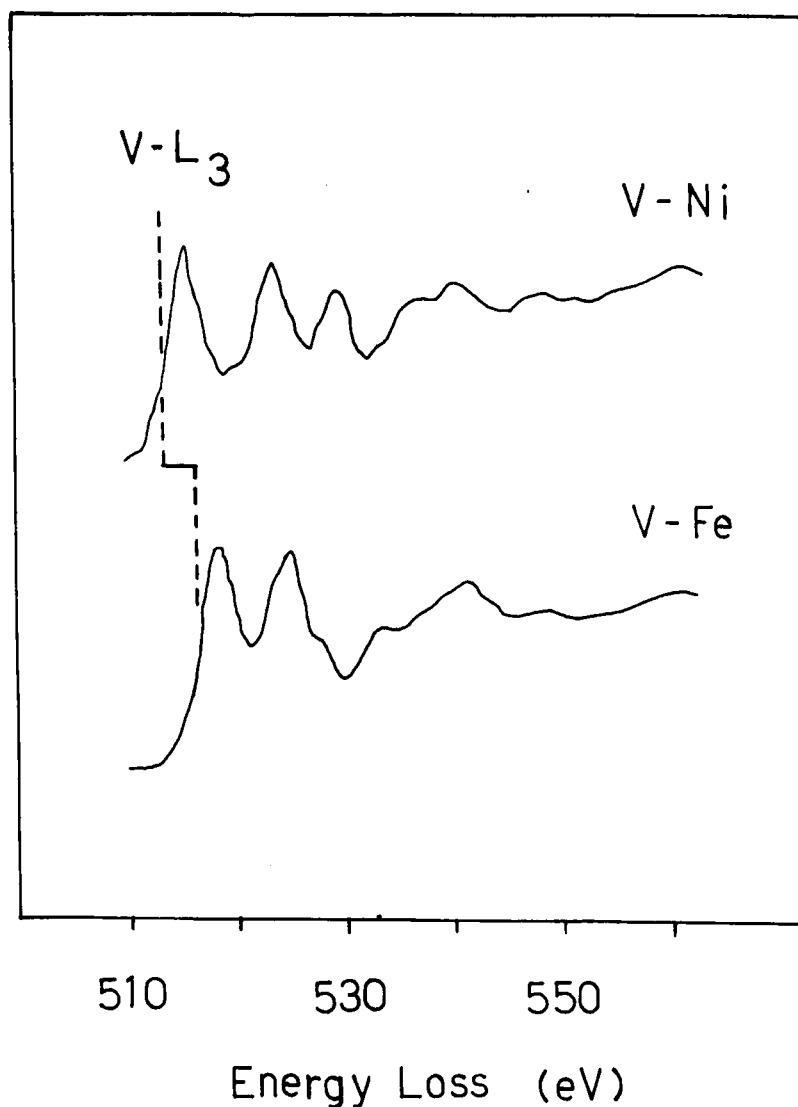


Figure 7 V- $L_{2,3}$ edge relative to V-Ni and V-Fe binary oxide phases.

In conclusion our ELNES measurements suggest V^{4+} in the V-Ni phase and V^{5+} in the V-Fe phase.

Crystal-chemical structure of binary oxide phases

On the basis of the obtained chemical, compositional and morphological data we tried to define the structure of the major crystalline binary oxide phases.

Fe-Ni phase (a cluster)

The particles in this cluster (Figure 3) amount to about 24% of the whole oxide phases; the Fe and Ni cations are present in the particles with a mean atomic ratio $Fe/Ni \approx 5/3$ and together account for 80% of the metallic cations present in all. V, Al, Cr and Zn were also detected in this phase with concentrations ranging between 2% and 5% (Table 1).

The Fe-Ni cluster particles have a polyhedral habit (Figure 8a), often showing regular edges. Their relative electron diffraction patterns (Figure 8b) show in general a pseudo-hexagonal symmetry, implying a likely monometric structure of the crystalline lattice.

It is interesting to observe that even if the atomic ratio Fe/Ni can range, in different particles, between 1/1 and 2/1, yet the atomic ration between trivalent cations B^{3+} (Fe, Al, Cr) and divalent cations A^{2+} (Ni, Mg, Zn) turns out to be practically constant and very close to the value $B^{3+}/A^{2+} = 2/1$ in all cluster particles.

These results suggest a crystalline monometric arrangement similar to that of spinel⁵, corresponding to an empirical formula AB_2O_4 , in which the divalent cations (A^{2+}) could be prevalently Ni, but also Mg or Zn, while the trivalent cations (B^{3+}) could be prevalently Fe, but also Al, Cr or V.

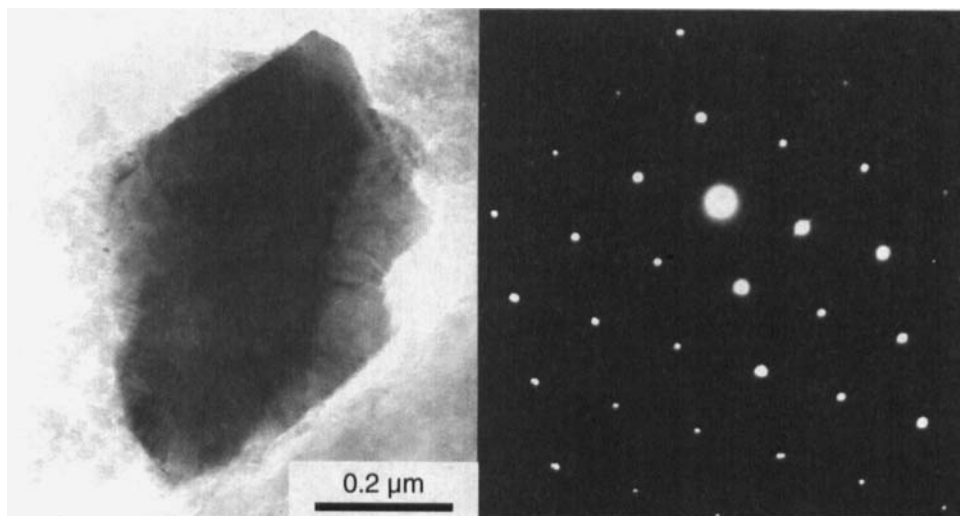


Figure 8 a) Fe-Ni crystalline oxide phase (TEM); b) the relative electron diffraction pattern.

V-Ni phase (b cluster)

The particles in this cluster (Figure 4) amount to about 22% of the whole oxide phases; the Ni and V cations are present in the particles with a mean atomic ratio Ni/V \approx 1/1 and together are 97% of the metallic cations totally present. Mg is sometimes present in this phase, but with a concentration not exceeding 2% (Table 1).

The V-Ni cluster particles show a lamellar habitat (Figure 9a) often with regular edges (quasi-hexagonal symmetry); their corresponding diffraction patterns suggest a well grown crystalline structure, yet they do not show a clear-cut symmetry (Figure 9b).

V, in this cluster, is present as V⁴⁺ (Figure 7). The above data are not enough to define a crystal-chemical structure, however the particle composition and the chemical state of Vanadium suggest a structure corresponding to an empirical formula: XVO₃, with the divalent cation (X²⁺) prevalently constituted by Ni²⁺, but sometimes replaced by Mg²⁺ or perhaps by V⁴⁺.

This kind of phase could be arranged in a hematite or even in a montroseite structure⁵.

V-Fe phase (c cluster)

The particles in this cluster (Figure 5) amount to about 11% of the whole oxide phases; the Fe and V cations are present in the particles with a mean atomic ratio V/Fe \approx 5/3 and together account for 80% of the metallic cations present in all. Ni, Al, Cr were also detected in this phase with concentrations ranging between 2% and 8% (Table 1).

The V-Fe cluster particles frequently show a lamellar habit (Figure 10a); the corresponding diffraction patterns suggest a well grown crystalline structure, yet they do not show a clear-cut symmetry (Figure 10b).

In this cluster V is present as V⁵⁺ (Figure 7), and it is noteworthy that the atomic ratio between V and the other cations (Fe+Cr+Al) is close to 1/1.

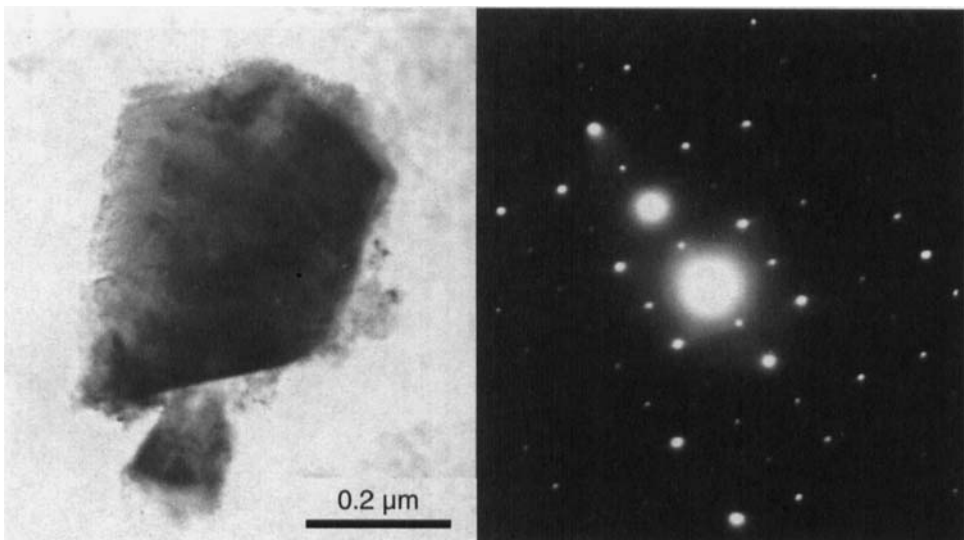


Figure 9 a) V-Ni crystalline oxide phase (TEM); b) the relative electron diffraction pattern.

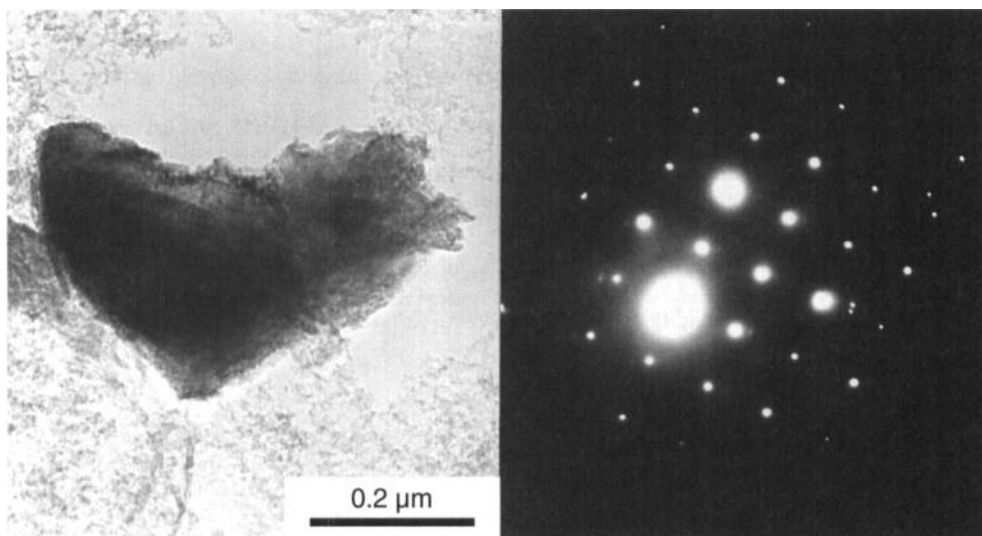


Figure 10 a) V-Fe crystalline oxide phase (TEM); b) the relative electron diffraction pattern.

Once again data are not enough to define a crystal-chemical structure, yet the particle composition and the chemical state of V suggest a structure corresponding to an empirical formula: $X(\text{VO}_4)$, with the trivalent cation (X^{3+}) prevalently constituted by Fe^{3+} , but sometimes replaced by Cr^{3+} or Al^{3+} .

CONCLUSIONS

In this work we utilised fly ash samples from the electrostatic precipitator of a fuel oil power plant.

It is well known that metals like V, Ni and Fe are contaminants always present in fuel oils⁶; however, the relative concentrations of the metals can change widely, depending on the geographic origin of the oils; for example in the ashes of fuel oils, Fe (as Fe_2O_3) can change from $\approx 8\%$ to more than 30% in weight; V (as V_2O_5) from less than 1% to $\approx 38\%$; Ni (as NiO) from less than 1% to $\approx 11\%$ ⁷.

Consequently, the absolute quantities of the different binary oxide phases (Fe-Ni, V-Fe, Fe-Ni) in fly ashes can probably change according to the origin of oil. On the contrary, the actual occurrence of the binary oxide phases (namely oxides in which two metallic elements amount to more than 80% ÷ 90% of cations) is not likely to depend on fuel oil composition but rather on the chemistry of the combustion process.

In the light of the structural data we obtained, the potential presence of an oxide phase with a spinel-like structure prevalently composed of Fe and Ni, and the finding that V is present in fly ashes with the highest oxidation states, V^{4+} and V^{5+} , in V-Fe and V-Ni binary phases, are both quite interesting observations from the environmental and toxicological points of view.

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