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Characterization of Fossil Oil Fly Ash and the Enrichment of the Contained Vanadium as V_4C_3 by High-Temperature Treatment

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A high-temperature treatment of fossil oil fly ash produced as combustion materials in oil-burning power plants is discussed with the aim of exploring the possibility of extracting vanadium compounds. As a first step, an attempt has been made to characterize the oxidation state of the vanadium in the powder, developing subsequently a thermal transformation in order to enrich the fossil oil fly ash in vanadium compounds suitable for its technological utilization. Several analytical techniques (EDS, ESCA, X-ray, atomic absorption) have been employed to characterize the vanadium content before and after various steps of a thermal treatment. The thermal treatment has been carried out with the aim of preparing higher value materials from the vanadium in the original state. A high percentage of V_4C_3 was obtained with the simultaneous depletion of the heavy metals present in the sample.

Introduction

In recent years the use of polymeric precursors to obtain carbides has attracted a great deal of attention. Metal atoms may be coordinated to the backbone of such precursors and a pyrolytic treatment can give carbides with good yield.[1,2] This yield is usually better than that attainable with the usually employed method; this consists in pyrolyzing a mechanical mixture of an inorganic derivative of the metal and graphite powder or carbon black.[3] It has been clearly established that a good efficiency is achieved by a more intimate contact of the metal atoms with the carbonaceous particles which favours the reaction kinetic.[1,2] The starting idea, on which the work described in this paper is based, was that a fossil oil is essentially a natural polymeric organic product with various differently linked heavy metal atoms.[4,5] An incomplete combustion in the oil-burning power plants represents, from our point of view, a first pyrolytic treatment giving the fly ash as a particulate already enriched in the heavy metals. Furthermore, the particulate contains an amount of carbonaceous substrate more than sufficient in intimate contact with the metal atoms. Its nature is such that these ashes, otherwise commercially scarcely remunerative, may become a useful source of metal derivatives, in particularly valuable chemical species.

A high-temperature process is here discussed concerning the possibility of a selective separation of vanadium compounds present in the fossil oil fly ash (FOFA) from electrofilters of power plants burning oil fuels. Vanadium compounds, either in the form of oxides or in the form of carbides, play an important role in the industrial field as oxidation catalysts,[6] materials for hardening steel,[3] and as plasma sprayed coatings.[7]

The first purpose of this work is to characterize the oxidation state of the vanadium in FOFA from Venezuelan oil, which is particularly rich in vanadium, and the second is to suggest a thermal transformation in order to enrich the FOFA in vanadium compounds saleable in the market with highest added value.

Some papers are reported where the chemical composition of the FOFA inorganic fraction has been determined.[4,8] Other papers are devoted to the evaluation of the thermodynamic properties of the therein contained vanadium oxides.[9−11] Finally, a number of papers are concerned with the enrichment of the vanadium content in the ash as pentoxide or ammonium

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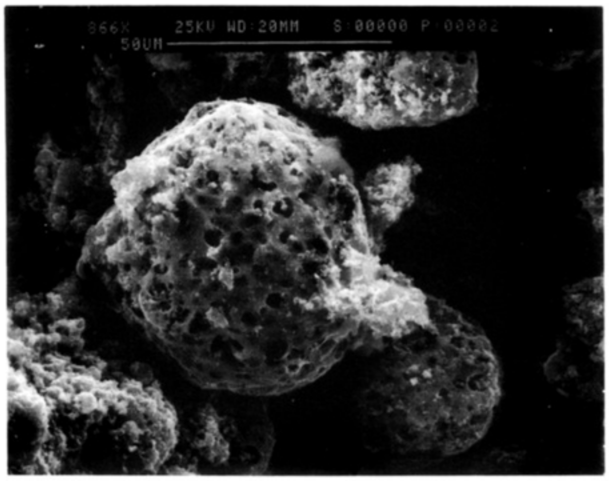

Figure 1. SEM microphotograph of the original fly ash.

vanadate by leaching and refining techniques.[12–18] A few works have been done on the metal recovery by thermal techniques[19] and none to our knowledge on the vanadium exploitation as carbide.

Our investigations deal with the characterization of vanadium in the FOFA sample performed by utilizing different nondestructive solid-state techniques (SEM, EDS, XRD, ESCA) and atomic absorption. Then the thermal transformations of the bonded vanadium were observed through the thermogravimetric technique.

Experimental Section

(a) Sample Characterization. For this study we used a FOFA sample representative of the firing conditions employed at a thermal power plant (ENEL-MILAZZO) before 1986, at that time stoked with an oil mixture containing a substantial contribution of Venezuelan "Laguna" oil. The sample has been morphologically analyzed with a SEM (Cambridge 100), revealing the aspect of cenospheres with spherical micro structure largely porous as shown in Figure 1.

The elemental analysis of both the original and high-temperature treated samples was carried out by atomic absorption and an electronic microprobe coupled with the scanning microscope. In the first method the samples were dissolved with a mixture of sulfuric, nitric, and perchloric acids according to the reported procedure.[20] Different amount of powders were employed on the basis of each element content.

A dilution ratio higher than 1:20 was never used in order to avoid further error source. The equipment used for atomic absorption (AA) analysis was a double-beam 460 Perkin-Elmer spectrophotometer. Sulfur was gravimetry determined as sulfate ion from its solution with chloric acid after fusion with Na_2CO_3. For EDS microanalyses, sample pellets were analyzed by a AN10000 85/S Link System with a ZAF 4 program.

A large number of EDS analyses were carried out in different parts of the samples in order to gain information about the average atomic ratio.

The elemental composition of the original sample was similar to that of other oil-fired fly ash samples examined.[7] The weight percent composition with respect to the sample dried at 300 K found by AA analysis is the following: V 7.88, Fe 1.30, Ni 1.26, Mg 0.93, Na 1.09, and Ca 0.25. The sulfur content, determined as above indicated, is 7.98 wt %. An error of ±0.05 is to be associated with the values. The sum of the determined contents is 20.7 wt % as the elements and 40.3 wt % as the respective oxides, where vanadium and sulfur have been assumed in the oxidation states 5, 4, 3 (as confirmed by XPS), and 6 respectively. Then the remaining 60 wt % may be attributed to unburned carbon, except for some residual water.

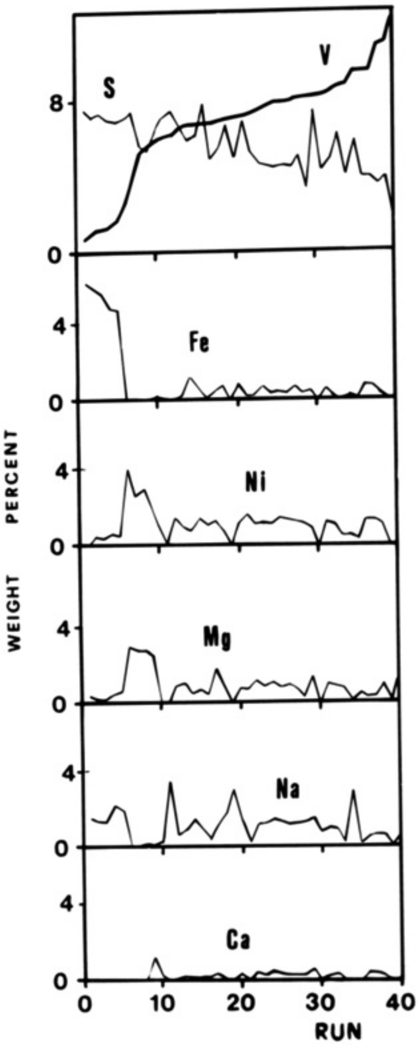

Figure 2. EDS elemental analysis of the FOFA powder. Ordinate: weight percent of the elements found in the active part of the sample. Abscissas: the 40 analytical aquisitions are ordered with respect to the increasing of the vanadium content.

Besides the large amount of vanadium and sulfur, the analyses revealed the presence of other heavy elements. This is also confirmed by the results of the EDS microanalysis shown in Figure 2 where on the ordinate the weight percents of the elements found in the active part of the microanalysis for each run are reported, ordered with respect to the increasing vanadium contents. In this way, it is possible to observe high iron content (>4%) only in the runs where vanadium and minor elements are much lower than the average. Such a result may be considered evidence that the presence of iron in the ashes comes from rusty parts of the industrial plant rather than from fired oil, whose iron content (≤36 ppm) cannot explain the total percent in the ashes. In any case, the results obtained are evidence for the large amount of vanadium compared to the remaining elements that justifies the opportunity of a convenient utilization of the waste material.

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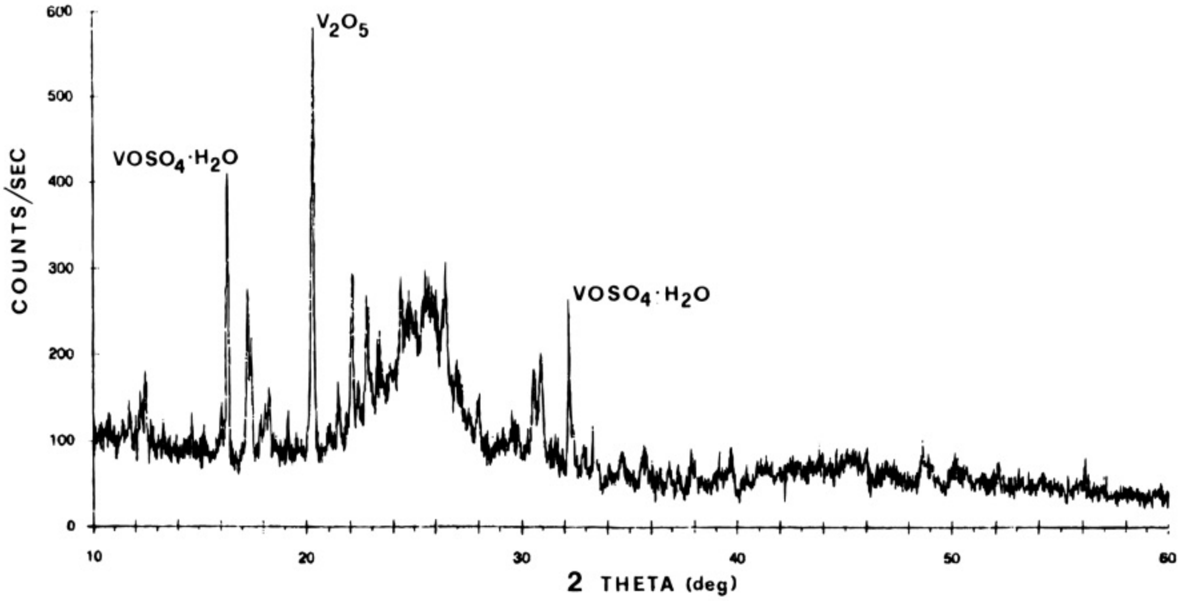

Figure 3. XRD analysis of the original FOFA.

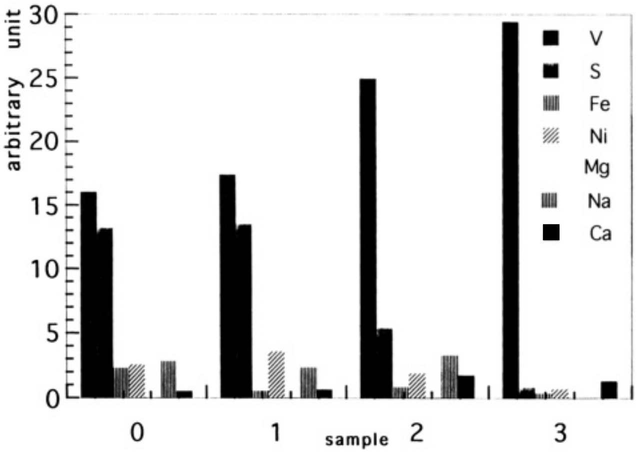

Figure 4. EDS quantitative microanalysis of the original and residual samples. Number 0−3 are referred respectively to the original FOFA and residuals.

(b) Vanadium Analysis. The percentage abundance of vanadium is about 7.8 wt % as the average of five values found by atomic absorption. This value agrees with that previously found by redox titration on samples from the same oil, reported by two of the authors.[20]

After this preliminary investigation on the composition of FOFA, our attention was addressed to the characterization of the chemical nature of the vanadium species. Several ash samples have been examined by the powder XRD technique. An automatic diffractometer was used with Cu Kα radiation. A comparison of the observed peaks (Figure 3) with the spectra of pure substances and with characteristic peaks reported in the Powder Diffraction Files[21] gives evidence for the presence of V_2O_5 and $VOSO_4 \cdot H_2O$, plus several unidentified peaks of lower intensity. No presence of carbon as graphite was revealed, while the broad peak around $2\theta \approx 25°$ should be assigned to amorphous carbon.

To reveal the vanadium oxidation state, XPS analysis was also attempted.

For this purpose an XPS-LHS10 spectrometer was employed on tablets samples, the used radiations being Al Kα (1486.6 eV) and Mg Kα (1253.6 eV). Different regions (C 1s, O 1s, V 2p, S 2s) were studied by using as refernce the bond energy of C 1s (284.6 eV).

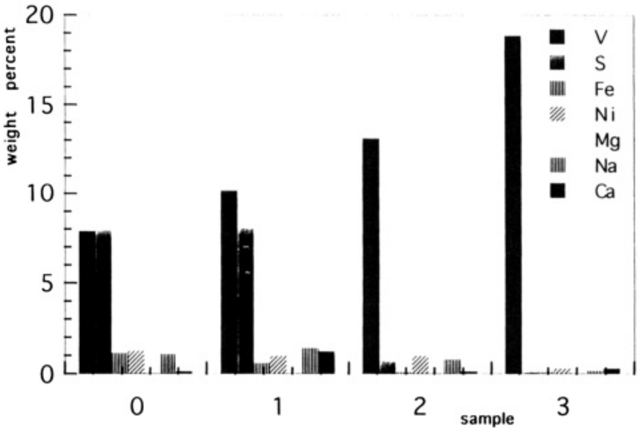

Figure 5. Atomic absorption analysis of the original and residual samples. Number 0−3 as in Figure 4.

Spectral analysis after smoothing and background subtraction showed the presence of sulfur as S(6+) and the absence of sulfur at different oxidation numbers. This result, though often reported in the literature,[20,22,23] is still surprising considering that the main gaseous product of sulfur combustion is certainly SO_2.

The well-known catalytic effect of the V_2O_5 in the ashes and the probable oxygen excess in the combustion, both favoring sulfur(VI) formation, cannot yet explain more than some unit percent SO_3 with respect to the total sulfur oxides produced. Nevertheless, SO_3 is likely to be prevailingly adsorbed by ashes and neutralized by basic components present therein, because of its far greater reactivity than that of SO_2. Detailed analysis of the evolved gases will be the object of future investigations. Concerning with the mass balance between the SO_3 produced and the basic oxides content in the ashes of the oil fired before 1986 at the ENEL-MILAZZO power station, the average value was 3% S and 0.02% ash. Assuming that 1% of total sulfur is oxidized to SO_3, the order of magnitude of concentration may be estimated for both reagents. Thus, the following reactions are possible:

$$(Na_2,Mg,Ca)O + SO_3(g) \rightarrow (Na_2, Mg, Ca)SO_4$$

$$V_2O_5(s) + SO_3(g) \rightarrow (VO_2)_2SO_4\ (s)$$

Ashes may also adsorb SO_2 from the gaseous phase, and then

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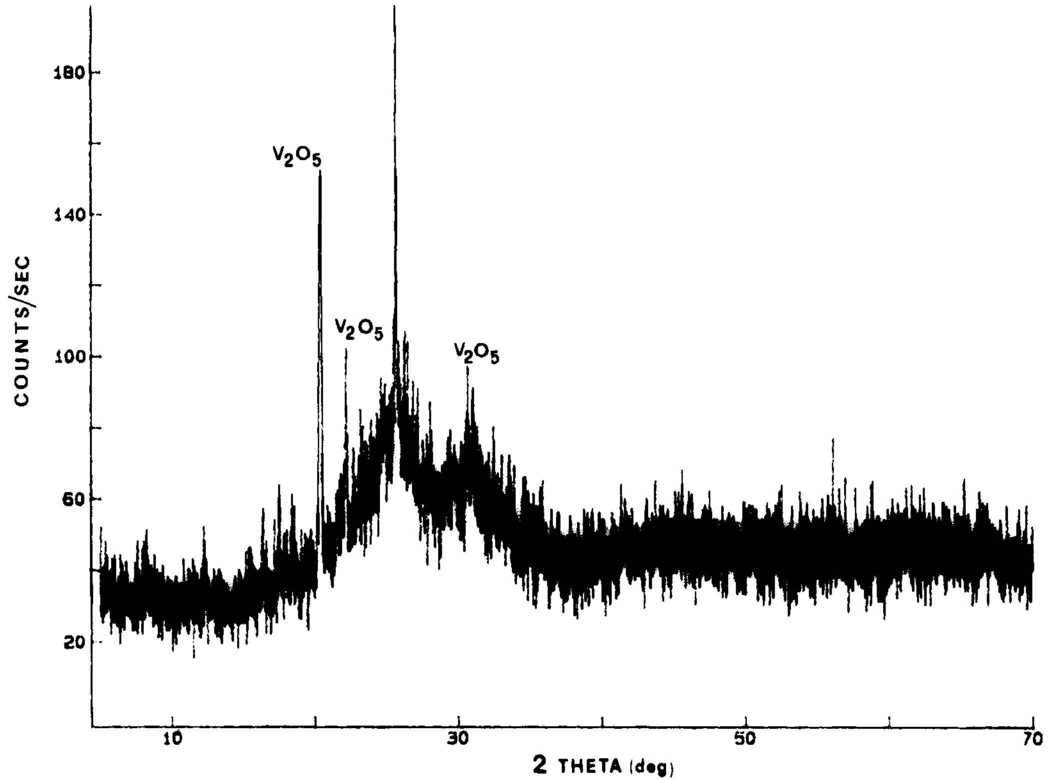

Figure 6. XRD analysis of the residual sample after step B of the thermal treatment.

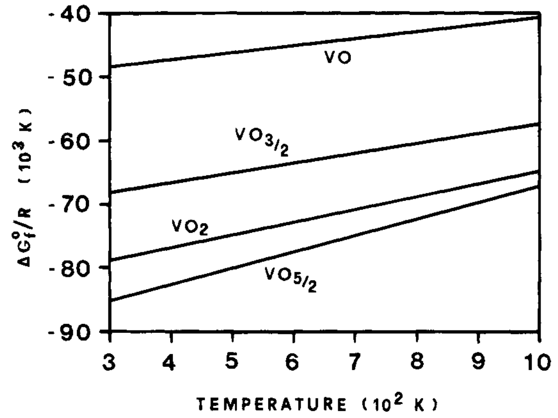

Figure 7. Standard free energy of formation from the elements of the vanadium oxides as a function of the temperature.

the following further reaction can occur:

$$(VO_2)_2SO_4(s) + SO_2(g) + 2H_2O \rightarrow 2VOSO_4 \cdot H_2O(s)$$

The above-reported sequence of reactions is also consistent with the following findings. Indeed, the vanadium valence state could be inferred from the three components V(5+), V(4+), and V(3+) with relative intensities of 62, 27, and 11, respectively, found from the evaluation of XPS spectra.

The presence of V(3+) could be due to the photoreduction effect during the recording of the spectra. We suggest that its presence is not due to chemical reasons, because an oxidation state of vanadium 3+ requires anions with a good ligand field, which is not a typical property of the sulfate. The carbon is present as carbon black, while the oxygen peak shows a strong component due to oxidriles and/or surface water besides an oxidic component. This confirms the presence of $VOSO_4 \cdot H_2O$ (in addition to V_2O_5) as stated by the other analyses and makes acceptable even a $VO(HSO_4)_2$ species formerly proposed by two of us[20] on the basis of a pH value of approximately 1 obtained by leaching the same ash sample with water.

(c) Vanadium Enrichment. An attempt was made to separate the low-density ashes from metal oxides and salts in order to obtain a vanadium-rich fraction. The flotation method using an organic liquid (iodomethane, density 2.8 g cm^{-3}) was performed, but a poor separation was obtained even with ultrasounds. The difficulty in the separation is due to the FOFA physical state, as evidenced in Figure 1; in fact its extreme porous structure offers an high surface tension which prevents wetting.

A thermal treatment is therefore suggested with a 2-fold aim: first to transform the vanadium from the original state into higher value compounds, second to eliminate the carbon excess.

The sample was heated in a thermobalance (Ugine Eyraud Setaram Model B-60)[24] in a platinum crucible under vacuum or under argon atmosphere (1 atm; the latter method was preferred in order to avoid the high expansion of a large amount of sorbed gases). In each experimental run a constant mass of the original powder (150 mg) was used to ensure both the sensitivity of the mass-loss measurements and the constant average of the composition. The results are reported in the following section.

(d) Thermal Behavior. Several thermal runs have been carried out from room temperature to 1800 K, with reproducible results. In all the thermograms recorded three main temperature ranges with different rates of weight loss, namely, A, B, and C are evident. At the end of each step the residual sample has been analyzed with SEM-EDS, XRD, and atomic absorption. The results are summarized in Figure 4 (EDS) and Figure 5 (atomic absorption), where samples analyzed after the A, B, and C weight loss (numbered 1–3) are referred to the original (number 0).

It is interesting to note that the two different experimental techniques lead to values in agreement taking into account

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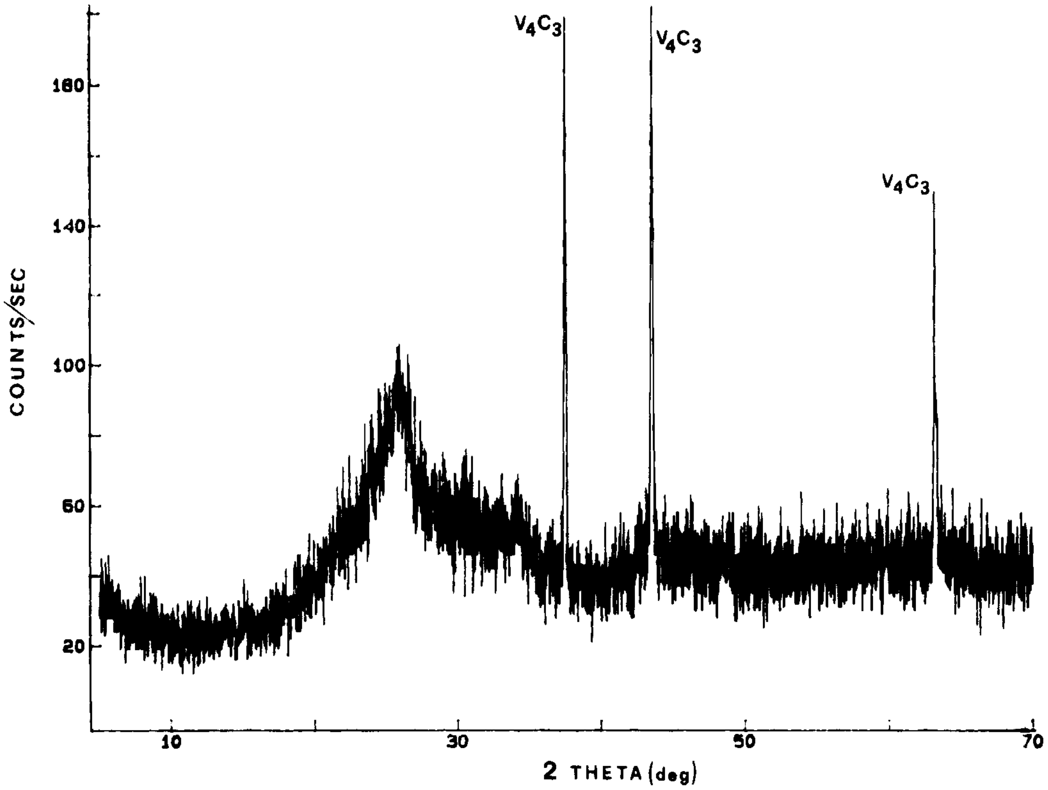

Figure 8. XRD analysis of the residual sample after step C of the thermal treatment.

that the EDS analysis is referred only to the active parts of the sample. The differential trends are the same in both analyses.

The phenomena observed in each step can be described in some detail as follows:

Step A: When the temperature was increased, starting from 320 K, a weight loss of about 13% due to releasing of the adsorbed water was observed. Quantitative analysis of the elements (sample 1 of the Figures 4 and 5) shows only a decrement of the iron content.

Step B: By further increasing the temperature, starting from about 670 K, an additional 19% lost may be related to the dehydration of the vanadyl sulfate and subsequent formation of vanadium pentoxide, through the following possible reactions:

$$2VOSO_4 \rightarrow V_2O_5 + SO_2 + SO_3$$

$$2VOSO_4 + C \rightarrow V_2O_5 + 2SO_2 + CO$$

both supported by the XRD analysis of the residual sample (Figure 6) and by the large drop of the sulfur content (see sample 2 in Figures 4 and 5). The first reaction can be considered possible on the basis of the hypothesis that the first step in the decomposition of $VOSO_4$ gives V_2O_4 (as some preliminary results seem to show). V_2O_4 would be subsequently oxidized to V_2O_5 by O_2 obtained from the catalytic decomposition of SO_3. A study finalized to the thermodynamics vaporization process of vanadyl sulfates is in progress.

The presence of only V_2O_5 is supported by a thermodynamic analysis carried out in order to evaluate the relative stability of the vanadium oxides as a function of temperature. Literature values of the thermodynamic properties of the most common vanadium oxides are reported in ref[25] or are available from a FORTRAN program named Thermo.[26] From these reports, the free energies of formation of the vanadium oxides are obtained and their values reported in Figure 7, where the thermodynamic stability of the vanadium oxides increasing with the oxidation number appears.

Step C: The last weight loss, starting from about 1000 K, is related to the formation of vanadium carbide by the reaction

$$2V_2O_5 + 13C \rightarrow V_4C_3 + 10CO$$

and/or

$$2V_2O_5 + 8C \rightarrow V_4C_3 + 5CO_2$$

The X-ray analysis confirms that V_4C_3 is the only vanadium carbide present in the solid residual sample (Figure 8). The reported reactions occur at high temperature, in fact is explained by thermodynamic calculations, performed with the aim of evaluating the feasibility of the transformation of V_2O_5 into vanadium carbide, support our assumptions.

Figure 9 shows the standard free energy of the reactions:

$$V_2O_5 + 7C \rightarrow 2VC + 5CO$$

and/or

$$V_2O_5 + {}^9/_2C \rightarrow 2VC + {}^5/_2CO_2$$

We can observe that the reported values of both reactions are negative for temperatures greater than 1000 K, so indicating that the above-mentioned reactions are thermodynamically favored in standard conditions. This can support the formation of the vanadium carbide observed in step C even if the obtained carbide (V_4C_3) is not exactly in the stoychiometric ratio 1:1.

An estimation of the V_4C_3 quantity achieved can be evaluated on the basis of the vanadium content determined by atomic absorption in the residual sample of the step C thermal treatment (Figure 5, sample 3). In fact, assuming that all the vanadium determined is in the V_4C_3 form (hypothesis con-

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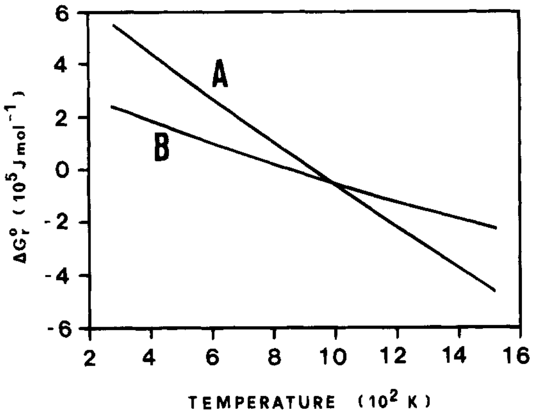

Figure 9. Standard free energy of the reactions: (A) V_2O_5 + 7C → 2VC + 5CO and (B) $V_2O_5 + {}^9/_2C \rightarrow 2VC + {}^5/_2CO_2$ as a function of the temperature.

firmed by X-ray analysis), calculation of the vanadium carbide content (about 22%) is possible. The enrichment in vanadium with respect to the pristine ash is evident.

Discussion and Conclusions

The analyses of the residual after each thermal step (A, B, and C) show evidence of the systematic decrease of the elements content S, Fe, Ni, Mg, Na, and Ca while the temperature is increasing. The loss of sulfur occurs at the step B according to the above-mentioned reactions. Fe and Ni probably react with the carbon monoxide formed in the previously mentioned reactions to give the volatile carbonyls $Fe(CO)_5$ and $Ni(CO)_4$.[27] Vanadium carbonyl does not exist in our experimental condition, because its formation requires the reduction of a suitable salt or complex. Concerning the disappearance of Na, it may be due to its volatility as Na_2O.[28] After step C the residue contains, in addition to vanadium, only magnesium and calcium, still in their original amounts.

We have verified that the excess and typology of cenospheres are essential in enriching the FOFA in vanadium and in efficiently transforming it in a high-value compound such as V_4C_3. A mechanical mixture of V_2O_5 and carbon black in proportions similar to those in the FOFA taken into consideration did not yield V_4C_3 with comparable purity and efficiency.

From the economical point of view, the described process appears very simple, not requiring particular procedures other than the achievement of relatively high temperatures. In this respect, a suitable utilization of the solar thermal technology (see, for example, our previous work[29]) could be employed with the advantage of reaching high temperatures at low cost with a nonpolluting energy source.

On the other hand a process should be set up which allows purification of the obtained vanadium carbide from the excess of carbon. We started to study, from both a theoretical and an experimental point of view, the potentialities in treating at different temperatures either the initial FOFA or the final mixture, with CO_2 or H_2. The treatment should transform the excess of carbon in CO or volatile hydrocarbons, respectively. However, also a mixture of carbon and V_4C_3 sufficiently enriched in vanadium carbide could be considered of value, for instance, in the process of hardening different steels.[3]

To conclude, while the final mixture already contains an appreciable quantity of V_4C_3, the settling up of an efficient method to eliminate the excess of carbon could really make commercially remunerative the treatment of FOFA to obtain V_4C_3 in pure form.

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