

**SYNTHESIS REPORT
FOR PUBLICATION**

CONTRACT No : BRE2-CT92-0120

PROJECT No : PE-5426-92

**TITLE : THE RECOVERY AND RECYCLING OF VANADIUM
AND NICKEL PRODUCTS FROM THE COMBUSTION
RESIDUES OF ORIMULSION AND OTHER FUELS**

**PROJECT
COORDINATOR : J.G. Sunderland, EA Technology Ltd.**

PARTNERS :

GfE UMWELTTECHNIK GmbH

INETI

MITSUBI BABCOCK ENERGY Ltd.

REFERENCE PERIOD: 1 NOV 1992 TO 1 NOV 1995

STARTING DATE : 1 NOV 1992

DURATION : 36 MONTHS



**PROJECT FUNDED BY THE EUROPEAN
COMMUNITY UNDER THE BRITE/EURAM
PROGRAMME**

DATE: MAY 1996

Introduction

Orimulsion is a relatively new power plant fuel which is finding slow but steady acceptance by power generators worldwide. It is the registered trade mark of PDV subsidiary Bitumenes Orinoco Bitor. The fuel is an emulsion of small droplets of natural bitumen in water. Water comprises 30% of the fuel which is maintained as an emulsion by the addition of a small amount of surfactant.

Orimulsion is considered a substitute for coal or oil in conventional power plants. Orimulsion fuel pricing is closely allied to the international coal prices at around £35 per tonne with transport cost additionally on top of this. The additional cost will depend on the transportation distance. The bitumen reserves are put at 186×10^9 tonnes, of which 45×10^9 are estimated to be recoverable. In this case one hundred 1000 MW power stations could operate for over 250 years. The older generation oil-fired power stations can be adapted to burn Orimulsion. Due to the high reserves, and competitive price there is an increasing interest in its use as a fuel. In addition it is also perceived as a strategic fuel so avoiding the dependence of relying on a single fuel source.

When Orimulsion is combusted a very fine ash is produced, much of which is carried up the power station flue stack with the flue gases. The installation of electrostatic precipitators allows the removal of 99.5% of the fine dust. The fine dust, or fly ash contains significant amounts of vanadium and nickel, which derive from the Orimulsion fuel oil. Nickel is a carcinogen and vanadium species classed as toxic substances. The toxic components present in the fly ash are highly leachable with water and, therefore, represent an environmental hazard, unless dealt with in a responsible manner.

Characterisation of the fly ash collected in the electrostatic precipitator, as noted above, demonstrated that the ash is a very fine material which before ageing has a maximum particle size in the region of $10\mu\text{m}$. The bulk density of the ash is correspondingly low, $\sim 100\text{kgm}^{-3}$. In order to allow safe handling without the hazard of dust inhalation the ash is normally conditioned following removal from the precipitator. The conditioning process involves mixing the ash with water prior to producing an extrudate or a granulated product. The granulated product has a bulk density of $\sim 1500\text{kgm}^{-3}$ and is dust free. Permission to store ash at a power station until sufficient has been stockpiled for disposal or upgrading, is possible-with the dust pre granulated product.

The fly ash collected in the precipitators is rich in vanadium (15% as vanadium pentoxide), nickel (3% as nickel oxide) and sulphates (50%)¹. In addition magnesium as hydroxide, oxide or other suitable magnesium salt is added to the Orimulsion or injected directly into the flame zone to help prevent boiler tube corrosion due to the presence of vanadium. The magnesium represents a high proportion of the fly ash (30% as magnesium oxide).

It can be calculated that forty 500MWe power plants are capable of producing 12,000 tonnes of vanadium per year, which is the present European consumption. In addition 3,000 tonnes of nickel can be recovered.

Vanadium until relatively recently has been recovered by pyrometallurgical techniques, which are expensive to operate. Hydrometallurgical techniques provide a

more cost effective method of recovering vanadium from vanadium rich fly-ashes, consequently Orimulsion as a new source of vanadium is reported in this short paper.

The vanadium and nickel present in the fly ash are highly leachable, Disposal to landfill can result in the leaching of the vanadium and nickel by rainwater. Consequently it is desirable to ensure that a sound technological and economic valorisation process is developed to handle this potentially toxic residue. Indeed it will allow:

- *The potential of an enormous new fuel resource to be realised.*
- *The recovery of valuable metals from a toxic waste.*

The work reported here has been carried out under the auspices of the Commission of the European Communities Brite-Euram II programme and describes the development of hydrometallurgical processes for the valorisation of Orimulsion fly ash,

The objectives of the project can be listed viz.:

- The identification of the most appropriate *economic* processes for the recovery of vanadium, and nickel from Orimulsion fly ash, and their conversion to chemical products of sufficient purity that they can be used, for example in the production of ferrovandium alloys.
- The construction and testing, at the laboratory scale, of the individual unit processes that will constitute the final integrated system.
- The production of a secondary solid residue(s), capable of being recycled.
- A comprehensive techno-economic assessment of the integrated plant design incorporating the most promising extractive and conditioning processes identified from the above,

ROLE OF THE PARTNERS

In formulating the Brite-Euram application it was clear that the consortium partners had to have the expertise required to develop and exploit the technology that was to be developed.

The consortium partners consequently provided the following mixed skill base:

1. EA Technology Ltd., U.K. Electricity utilisation and the power generation industry.
2. GfE Umwelttechnik GmbH., Germany, an international metallurgical company involved in the production of vanadium pentoxide and vanadium chemicals,
3. Mitsui Babcock Energy Ltd., U.K. an international engineering business involved in all aspects of process plant for power stations.
- and 4. INETI, Portugal partner involved in hydrometallurgy, materials and environmental science and the associated technologies.

DESCRIPTION OF THE RESEARCH WORK

The aim of the research work programme was to recover the metals from the fly ash in high yields and with a view to minimizing the amount of residues and waste streams produced in the process. The main tasks can be summarised as follows:

- ❑ Characterisation of the vanadium/nickel containing fly ash residues
- ❑ Extraction of vanadium and nickel using aqueous leachates
- ❑ Separation of vanadium and nickel from the leachate
- ❑ Purification of vanadium and nickel
- ❑ Process improvements using solvent extraction
- ❑ Secondary waste treatment and/or recycling
- ❑ Techno-economic process information
- ❑ Reference design for the treatment of power station fly ash residues

Physico-chemical characterisation of fly ashes

Mitsui Babcock took responsibility for the physico-chemical analysis.

The fine electrostatic precipitator dusts are produced in large quantities and, being finely divided, they are attractive as the feedstock from which vanadium and nickel can be extracted.

CHARACTERISTICS OF ORIMULSION COMBUSTION RESIDUES

Chemical Composition

As discussed above, the work has concentrated on the fly ashes collected from the electrostatic precipitators. The basic chemical analysis data for a number of fly ash samples are listed in Table 1. Although Orimulsion is a relatively consistent fuel, and the ash composition is reasonably constant, the chemical composition of the electrostatic precipitator dusts can vary significantly from site to site and from time to time at a particular site.

Typical ash composition is as follows:

Table 1

calcium	40 - 80	mg kg ⁻¹ of fuel, as received
magnesium	430 - 850	mg kg ⁻¹ of fuel, as received
nickel	60 - 180	mg kg ⁻¹ of fuel, as received
sodium	50 - 110	mg kg ⁻¹ of fuel, as received
vanadium	290-450	mg kg ⁻¹ of fuel, as received
iron	10 - 20	mg kg ⁻¹ of fuel, as received
chloride	90-200	mg kg ⁻¹ of fuel, as received

Examination of the data presented in Table 1, indicates the following important variations in composition of the electrostatic precipitator dusts:

a) The unburned carbon contents of the dusts are dependent on the quality and efficiency of combustion. In the case where very good combustion conditions generally apply, the unburned carbon content of the electrostatic precipitator dusts is invariably less than 2% by weight and generally less than 0.5%. Where combustion conditions are not effectively controlled, unburned carbon levels in the range 3 - 6% by weight have been measured.

b) The dusts are completely dry when collected hot from the electrostatic precipitator hoppers. They do, however, have a tendency to absorb moisture from the atmosphere. The handling behaviour of the dusts are affected by adsorbed moisture particularly in pneumatic systems. The moisture content of a particular sample clearly depends on its handling and storage history, and moisture contents up to 10% by weight have been measured. There is a tendency also for hydration of the $MgSO_4$ in the dusts to $MgSO_4 \cdot 6H_2O$. This combined water is released from the dusts at temperatures in excess of 100°C.

Clearly, the reaction of the dusts with atmospheric moisture and the reactions which occur when the dusts are mixed with water to produce the extrudate material are important in the current context, and they have been the subject of a separate, more detailed study.

c) The Orimulsion combustion residues are also rich in sulphates. These are formed by sulphation of the metal oxide species by reaction with SO_2 and SO_3 in the furnace chamber, the boiler and the electrostatic precipitator, and, as such the degree of sulphation is dependent on the combustion conditions, the excess air level and the boiler configuration. There is also evidence that the presence of vanadium can act as a catalyst on the oxidation of SO_2 to SO_3 and hence can increase the level of sulphation. The extent and form of the ash deposition on boiler surfaces may also influence the extent of sulphation of the gas-borne particulate material.

d) As indicated above, the Orimulsion ash and the combustion residues are relatively rich in a number of specific metal oxides and sulphates. These can conveniently be subdivided into three categories:

1. The transition metals, principally vanadium, nickel and iron occur in the form of porphyrins, complex high molecular weight organo-metallic compounds which form part of the hydrocarbon structure of the Orimulsion. Since this is a natural product it is subject to variation. The Orinoco deposit is, however, well characterised and the limits of this variation are well understood. The ranges of values listed earlier in this report for metals contents of Orimulsion apply. Measured values for the samples of electrostatic precipitator dusts lie substantially in the following ranges:

V_2O_5	13-22%	by weight
NiO	2 - 3.40	by weight
Fe_2O_3	0.5- 3.5%	by weight

These values are clearly dependent on the unburned carbon, moisture, and sulphate contents of the ash. On a carbon, moisture and sulphate-free basis, the V_2O_5 contents are relatively consistent and lie in the range 28 - 30% by weight,

2. Hydrocarbon deposits are almost invariably associated with salt waters in the geological formations in which they are found. This is also true of the Orinoco deposits, and although the raw hydrocarbon is desalted and fresh water is introduced in the Orimulsion production process, the fuel does contain small quantities of soluble calcium, sodium and magnesium compounds, normally at concentrations in the range 10-100 $mg\ kg^{-1}$ fuel, as fired.

3. In its current formulation, Orimulsion is stabilised using a specially designed additive package which contains a magnesium salt. The Mg content of the fuel is currently in the range 430 - 850 $mg\ kg^{-1}$, as fired, and the MgO content of the electrostatic precipitator dusts is in the range 27 - 38% by weight. This is clearly dependent on the particular surfactant formulation employed and may change with time.

X-Ray Powder Diffraction Analysis

The X-ray powder diffractograms obtained with the electrostatic precipitator dusts were very complex but were similar in most important aspects. The following crystalline phases have been positively identified as being present in both cases:

MgSO ₄	major phases
MgSO ₄ .6H ₂ O	
MgO	significant phases
Mg(OH) ₂	
MgO.V ₂ O ₅	minor phases
3MgO.V ₂ O ₅	

A complete assignment of all of the reflections on the diffractograms did not prove to be possible. Samples exhibited eight common reflections (weak or very weak) and in one case a further two reflections (weak) were in evidence these defied identification. This is not surprising, since vanadium chemistry is very complex and has not been exhaustively studied. The reflections which remain unassigned, however, were weak or very weak, i.e. they represent minor phases.

The results of the X-ray powder diffraction are in good agreement with the chemical analysis data in that the significant crystalline phases which have been identified contain MgO, SO₃ and V₂O₅. The major phases are anhydrous MgSO₄, the hydrated MgSO₄.6H₂O and the unreacted MgCO₃ and Mg(OH)₂ species.

Physical Characteristics

The dry, fresh dusts collected directly from the electrostatic precipitator hoppers are very fine and contain a significant level of submicron material. Particle size data indicate that in excess of 50% of the material by weight had an aerodynamic diameter less than 1 micron,

Absorption of atmospheric moisture by the electrostatic precipitator dusts results in the hydration of $MgSO_4$ to form $MgSO_4 \cdot 6H_2O$. This has been confirmed by X-ray diffraction analysis. A degree of recrystallisation and agglomeration occurs within the dusts with time,

Table 2 shows the chemical composition of samples collected on different dates and from two power plants. There is a significant variability in the composition of the two fly ashes. This is not a problem and is easily circumvented provided the fly ash is analysed on a daily basis so that the appropriate stoichiometric amount of leachant can be added. The carbon content of the ash is seen to vary and reflects the different fuel to oxygen ratios used in the two plants,

Table 2. Analysis of two samples of fly ash obtained under different fuel :air ratios.

Sample	EXTRUDATE SAMPLE 1	EXTRUDATE SAMPLE 2
Constituent	% w/w	
V_2O_5	12.0	16.0
Fe_2O_3	1.2	0.4
CaO	1.1	2.0
Mgo	19.7	18.5
NiO	2.0	2.0
Na_2O	2.1	1.6
S03		32.5
Moisture	26.0	18.4
Unburned C	0.1	1.7

LEACHING OF FLY ASH

The major chemical component of the fly-ash is vanadium, present as a magnesium-vanadium sulphate. This has a significant market value which can be used to offset the cost of a treatment plant. Its recovery as a water soluble vanadate as a first step from the fly ash is, therefore, attractive, since it can be used as the precursor for conversion to more valuable vanadium compounds.

The first step in the upgrading process involves leaching of the fly-ash to recover vanadium, nickel, iron and magnesium. Water, sulphuric acid, sodium hydroxide and ammonia/ammonium chloride have all been examined as suitable leachants. Since sulphate formed a major component of the fly ash sulphuric acid was selected as the leachate.

During the early stages of the project the Orimulsion fly ash available was changed from a dust to an extrudate, and very late in the project a granulated material was produced. It was necessary, therefore, to assess the leachability of the extrudate and compare these with the results already obtained with the dust and subsequently with the granulated material. **GfE** and **INETI** undertook this part of the work.

EA continued with the dust (later the granulated material) since it had been determined from the preliminary leaching studies that the two physical forms gave virtually identical results.

The leaching process was studied by EA, GfE and INETI. It was clear that in the case of sulphuric acid as leachant there was a choice between using stoichiometric amounts of sulphate, expressed as H_2SO_4 to leach the metals from the ash or to use an excess of sulphate. GfE in an initial economic analysis concluded that as long as 91% of the vanadium was recovered this would be sufficient justification for developing the recovery process further.

Consequently leaching was carried out with the required stoichiometric amount of acid. On a routine basis analysis of the fly ash is necessary so that the sulphate deficit can be defined. This also had the advantage that the volume of solution to be disposed of or treated in the process is kept to a minimum.

Experimental parameters such as temperature, leaching time and solid liquid handling were all examined. Solid-liquid separation is a sensitive operation. Indeed the very fine and non-crystalline nature of the solids makes the filtration operation very slow if appropriate flocculants are not used. Consequently a range of flocculants were examined and the optimum flocculant additive defined.

These initial results were obtained in batch leaching experiments. This was extended by INETI to include exhaustive continuous leaching studies.

The merits of batch and continuous leaching have been examined in detail. Although there is no obvious downside to either of the extraction operations it was concluded that on a industrial scale batch leaching is preferred.

Leaching yield and Recovery of Vanadium as a compound

Table 3 is a summary of the extraction and recovery process results. It can be seen that vanadium is leached from the fly-ash with an average of 90% efficiency. The majority of the vanadium is removed as a vanadium compound,

Table 3 Results for the extraction and recovery of *vanadium*

	Expt 1	Expt 2	Expt 3	Expt 4	Expt 5	Expt 6	Expt 7	Expt 8	Average
Leachate									
Concn g/l	14.85	16.08	14.79	15.66	18	17.4	15.28	17.3	16.17
Mass g	29.7	32.16	29.58	31.32	36	34.8	30.56	34.6	32.34
% extracted	81.59	88.36	81.26	86.04	98.9	95.6	83.95	95.05	88.87
Final filtrate									
Concn g/l	1.5	0.653	0.83	0.18	0.31	0.265	0.305	0.26	0.53
Mass g/l	2.985	1.24	2.49	0.477	0.775	0.557	0.71	0.53	1.22
% of total	10.05	3.84	8.4	1.52	2.15	1.6	10.28	1.5	4.918
Product									
Mass g	25.43	31.38	27.38	25.08	33.8	28.49	32.4	26.36	25.07
% of compd.	50.2	25.3	21.01	12.07	45.07	33.46	46.93	36.9	33.87
% of total	55.6	97.61	92.56	79.8	93.88	81.86	106	106.6	92.98

Different vanadium compounds were synthesised following the initial leaching step and each process route carefully considered in terms of:

1. the ease of synthesis
2. recovery yield of the vanadium in the synthesised compound
3. the purity of the vanadium compound allowing fewer final purification steps
4. the economics of the selected synthesis

and 4. the resulting process stream and treatment required to allow recycling or discharge to drain/sewer.

Following this analysis two vanadium compounds were identified as suitable for more detailed consideration. Following the detailed considerations one vanadium compound was selected for a detailed analysis. This compound was used as the basis for carrying out the techno-economic analysis,

In the study, details of how the alternative vanadium compounds could be synthesised were documented so that if required an alternative vanadium compound could be synthesised, depending on local requirements and availability of alternative chemical reactants.

Recovery of nickel as metal or as a compound

Although nickel is present in the fly ash to the extent of 2%, compared with vanadium, 7-9% , it is also a valuable material in economic terms. In terms of its metal price this has varied over the three years of the project from \$2.4 per LB to \$4 per lb. This is in contrast to the vanadium price which has varied from a low of \$1.2 per lb up to a high of \$4.3 per lb.,

The solution arising following the synthesis of the vanadium compound(s) contains nickel and magnesium. A typical nickel bearing solution (table 4) has the following composition:

Table 4. Concentration of metals in solution following recovery of vanadium

Element	Concentration g/l
Ni	4-5
Mg	25-30
V	0.4-0.8
Fe	0.05-0.1

Depending on whether nickel is required as metal or a nickel compound, it is necessary to implement a *specific process route* to recover the vanadium. The resulting process stream can be electrolysed to recover a high purity nickel foil which can be sold into the nickel market and used to help offset the processing costs. A typical process flow sheet is shown in figure 1. An alternative process route is

favoured, however, this involves the precipitation of a nickel product that can be sold into the secondary nickel market.

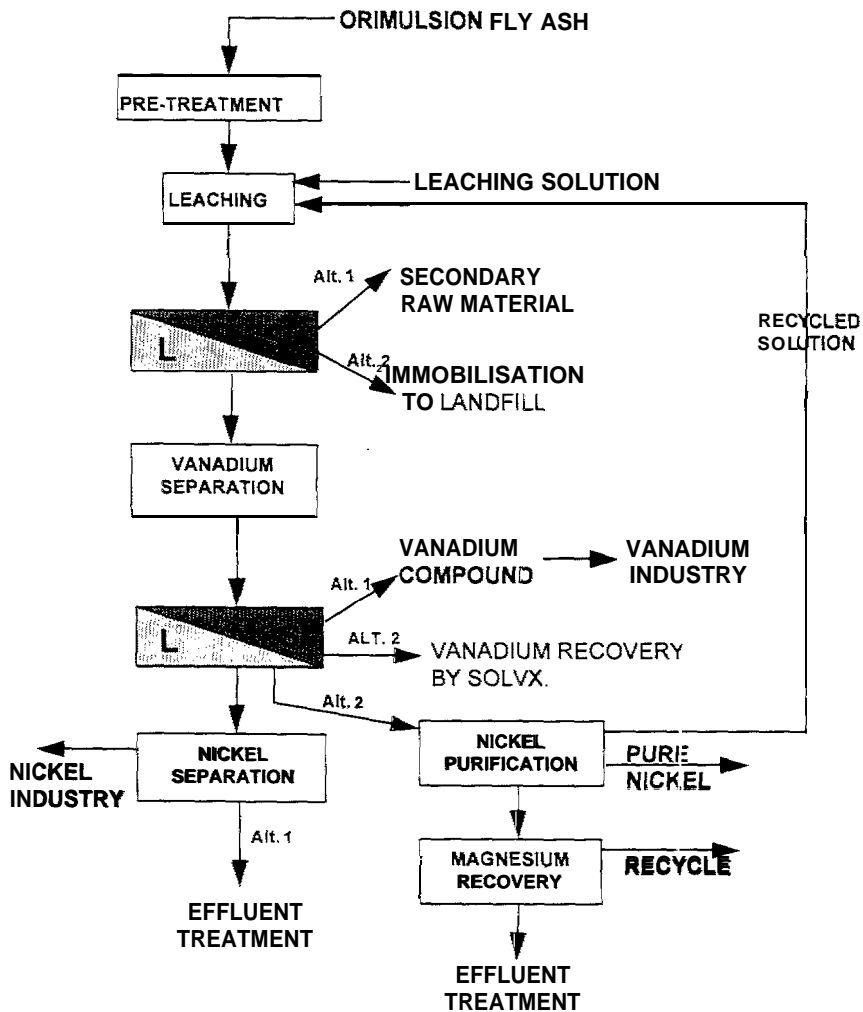


Figure 1. Flowsheet of the developed precipitation process -including process streams for extracting by solvent extraction.

Nickel is a toxic chemical and has a waste stream discharge consent limit of 2ppm. Consequently it is essential that the nickel content of any effluent stream is handled and dealt with in a responsible manner. The synthesis of the nickel compound and its recovery by filtration results in a filtrate which is low in nickel (2-10ppm under optimum conditions). By simple pH adjustment the concentration of nickel in solution can be reduced to - 3ppm and on mixing with other process waters passing to drain easily meets any discharge consent limit.

As with all new developments process improvements are always being sought. In the case of the work described here this project is no exception and the use of solvent extraction for recovering vanadium, nickel and magnesium from the different synthetic process streams is desirable. Theoretically solvent extraction is capable of allowing the recovery of individual metal salts in the pure state, and limiting the loss

of toxic metals from a process. Its application in the recovery of metals, from potentially “waste” materials has not been widely applied, but where an upgrading plant is only part of a large capital expenditure there is the potential to exploit the strengths of solvent extraction. The use of solvent extraction to the recovery of vanadium, nickel and magnesium, therefore, investigated in detail.

The preliminary test work carried out consisted of the screening of a range of extractants using 150ml capacity separating funnels. The use of alternative diluents, and modifiers to aid the extraction and stripping procedures were also incorporated as part of the initial work.

The most promising extractant/modifiers/diluent mixtures were evaluated using the McCabe-Thiele graphical method to determine the number of extraction stages needed to obtain raffinates containing no vanadium (or very low levels) and the extent to which the nickel and magnesium remained in the original acidic leachate.

Test work on the optimisation of sulphuric acid stripping of the vanadium from the loaded solvent, and removal of impurities accumulated in the solvent, such as iron was examined. The use of alkaline regeneration in a side stream of the organic after the acid stripping operation was also investigated.

Alternatively, direct pH control during extraction, to reduce the number of stages, and to obtain raffinates of higher quality was also studied. These studies were carried out with the solvents previously chosen.

It has been demonstrated in the work that with the appropriate choice of solvent mixtures it is possible to recover each of the metals selectively. The metal salts that are recovered are very pure. In the case of nickel, nickel sulphate can be recovered as a concentrated solution, $>80\text{g/l}$, from which nickel can be recovered by electrodeposition. Following the electrodeposition step the barren solution can be recycled to the stripping stage.

There is no loss of the magnesium in the solvent extraction process. This is recovered and converted into a magnesium compound suitable for returning to the Orimulsion as a corrosion inhibitor.

With the data obtained from the McCabe - Thiele diagrams determined previously it was possible to propose a reaction scheme for the continuous solvent extraction of vanadium from the oxidised leaching solution in a counter-current flow unit. A typical counter current box mixer settler is represented in figure 2.

The loaded strip solutions had no nickel or magnesium, so that separation of these two metals from vanadium was achieved. The yield for vanadium recovery was at least 96.94%.

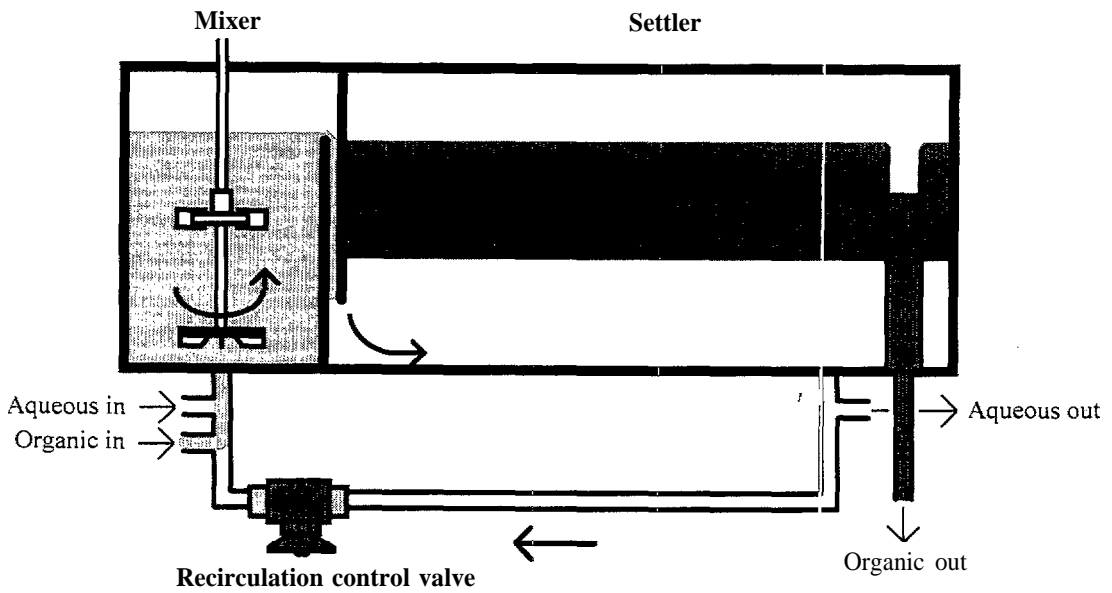


Figure 2- Representation of a mixer and a settler for continuous counter current flow solvent extraction and stripping.

A typical outline flow sheet of the alternative solvent extraction routes developed for the recovery of the metals present in the Orimulsion combustion residues is shown below in figure 3,

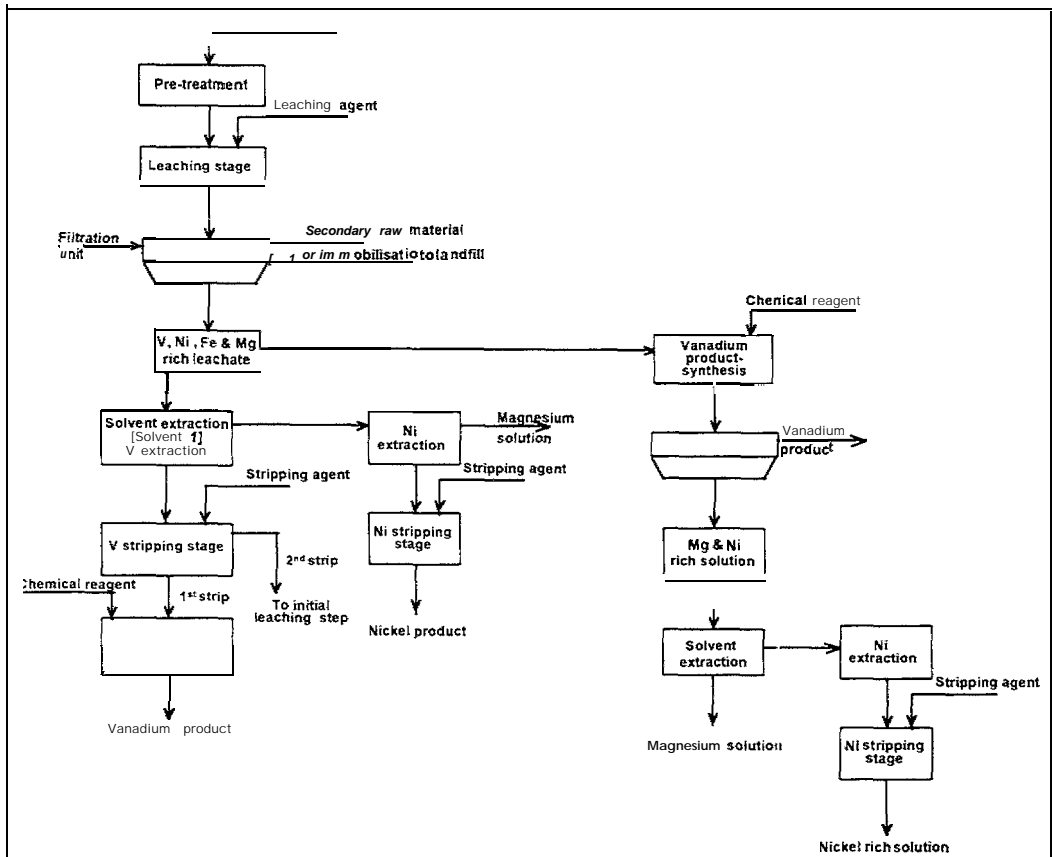


Figure 3

Solvent extraction requires a higher investment and is technically more demanding, and a more difficult operation to control than the precipitation route described above. Nevertheless it does have advantages. The higher value of the final product - concentrated nickel sulphate that can be electroplated - and the fact that only environmentally benign effluents are obtained are important benefits.

Vanadium and iron **removal** from the leachate by solvent extraction is a highly efficient operation. By applying solvent extraction in other extraction/stripping steps it is possible to separate nickel and magnesium. The nickel can be purified and concentrated producing a nickel solution (e.g. sulphate) at up to 80g/l. In addition, the remaining magnesium can also be processed (also by solvent extraction) in order to be recycled to the Orimulsion production stage. No valuable metals are lost and no harmful effluents are lost. This is a clean process, only perhaps less favorable due to the more complex and expensive technology that involves.

Throughout the project great emphasis has been placed on minimizing waste solids and streams. The solid residues that remain after the leaching step represents < 1 0% of the initial weight of fly ash. This is best **used** as a sweetener added to other vanadium sources in a pyrometallurgical process to produce ferro-vanadium. In addition a strategy has been devised for handling the final magnesium rich final effluent.

Techno-economic assessment and exploitation of the technology

A full techno-economic assessment by **Matsui Babcock** for a 2000MW_e power station, producing 30 tonnes of Orimulsion fly ash per day, and situated adjacent to a power station with FGD, has been carried out for the technology developed for the selected vanadium and nickel recovery process.

A 20 kg scale pilot plant is available at, **EA Technology**, for carrying out initial trials for potential clients. Following successful laboratory pilot trials larger industrial scale trials (1 0's of tonnes) can also be offered by **GfE** if required. Solvent extraction process technology for recovering vanadium, nickel and magnesium salts can be undertaken by **INETI**

It should be stressed that the technologies developed offer a flexible approach. Alternative vanadium and nickel products can be synthesised to meet local requirements.

The number of power station conversions to burn Orimulsion is increasing, so that fly-ash upgrading will be required to prevent toxic metal loss into the environment. The technology developed by the consortium under a Brite-Euram funded work programme represents a fully developed process technology.

Acknowledgments

This Consortium members gratefully acknowledge the financial support provided by the European Community within the Brite Euram H, Industrial and Materials Technologies Programme under **Contract Number BRE2-CT92-0120 & Project Number BE-5426-92.**

References

- 1 A paper "The Recovery and recycling of vanadium and nickel products from the combustion of Orimulsion and other fuels" was presented at the Brite-Euram E.C. Workshop June 13-14, 1995, held in Freiberg, Germany by Dr. Krummen.
- 2 Dr. Rodrigues presented a paper "The Recovery of Vanadium of Nickel from Orimulsion Combustion Ashes" at the "Second East-West Workshop on Chemistry and Energy" held in Sintra, Portugal, 1995.