

Shiv Vijayan and V.I. Lakshmanan

## 8.1 Introduction

The separation and removal of metals of interest from various matrices such as ores, or aqueous or organic solutions containing those metals can be achieved by a variety of metallurgical processing methods. The main goal in processing is to remove the metals of interest as selectively and economically as possible while permitting the final discharge of all the liquid, solid, and gaseous effluents generated from the processes to the environment. The effectiveness of a process is judged by the separation efficiency, that is, the ratio of metal concentration in the metal-depleted effluent to metal concentration in the feed matrix. Effectiveness is also judged by the reduction in volume achieved between the original material being processed and the final effluent requiring safe management as waste material. For example, metal separation efficiency in the range of 90–99 % and volume reduction factors in the range of 10–1000 are typical requirements in many applications involving solid and solution matrices.

In any metal separation process initiative, the end-deliverable is characterized by a set of

performance aspects (PA) related to the implementation and operation of the overall process system. The common performance aspects are capital and operating costs (or life-cycle cost), and duration from concept identification to system start-up. In addition, there are other aspects, which impact cost and duration but are difficult to quantify up front in terms of these measures. These could be safety (measured through operating experience and consequences of system failure), ease of compliance with regulations, perceived environmental impact, utilization of existing resources (equipment and personnel), etc. A consensus on key aspects for such an initiative is generally arrived at among technology specialists, finance controllers, licensing experts or regulators and customer/stakeholders.

A structured approach for process selection from various options, which is discussed in this section, is based on a familiar, common sense approach to decision-making without bias. This simple approach can be considered as an effective and innovative tool for the process selection team. Such a simple but innovative approach would benefit the decision makers to arrive at a logical outcome in a consistent manner. Application of innovative approaches on all facets of the operation is essential in today's globalization of commodity markets, in particular the metal markets, in order to remain competitive and sustainable in the long term (e.g., Lakshmanan 1992).

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S. Vijayan (✉) • V.I. Lakshmanan  
Process Research ORTECH Inc.,  
2350 Sheridan Park Drive, Mississauga, ON,  
Canada, L5K 2T4  
e-mail: [shiv.vijayan@gmail.com](mailto:shiv.vijayan@gmail.com)

## 8.2 Methodology

This section describes the first of a two-stage structured evaluation of process options to arrive at the best process for removing one or a group of metals of interest from a solid or a solution as the feed to the process. To arrive at the best process option, it is recognized that an integral logical analysis of the issues and their impact on performance is essential. The approach used here was evolved from the principles embedded in the Theory of Constraints Methodology (Goldratt 1999). The methodology involves a two-stage approach. In Stage 1, a four-step analysis is used (e.g., Tennankore and Vijayan 1999), namely, identification of options, identification of key performance aspects and associated measures, assessment of impact of the options on the performance aspects, and an overall assessment. A simple scoring method based on “1,4,9” (“low, medium, high” preference) is used to quantify the impact of the options on key performance aspects. The overall score is obtained through appropriate weighting of the score for individual performance aspects and is then used to short-list the preferred options for further detailed evaluation to arrive at the best option.

If weights for performance aspects are selected and fixed, a short list of options can be deduced for further detailed evaluation of impacts on the performance aspects to arrive at the best option.

## 8.3 Methodology Application

Several approaches essentially based on common sense performance factors have been and are being used to select the most promising option from a list of options. However, a structured approach discussed in this section is expected to provide an initial selection of a short list of options without bias, which can be used as the basis to perform sensitivity analysis of the effects of the performance factors, and to arrive at a consensus by the process selection team.

To illustrate the structured approach as an innovative and effective method to process selec-

tion, as an example, process options for vanadium extraction to produce marketable product(s) were considered. In order to evaluate the processes options for this example, the following key assumptions have been made.

- The need for vanadium extraction from flyash as the feedstock is justified on the basis of quantity, availability, and resource demand (and an opportunity to create value from industrial waste)
- Through a search of information in published literature, five process options were considered available and selected
- The recovered product and by-products were justified to have sufficient market
- There were no legacy or political issues applicable
- The goal for the methodology application and evaluation of the process options do not attest or recommend one or more processes. Any opinions and analysis may only be considered as an exercise for methodology considerations, and should not be interpreted as final answers to a vanadium recovery process for implementation.

Process options for the recovery of vanadium from flyash, and the selection of a short list of the most processing options by using the process selection methodology described in Table 8.1 are analyzed in the following section.

### 8.3.1 Methodology Application: Flyash and Its Utilization

The utilization of a waste material such as flyash as the secondary resource for vanadium is important not only for saving the raw material resource but also for closing the vanadium cycle, thus reducing the environmental impact (Xiao et al. 2010).

Flyash is generated as a waste effluent (e.g., thermal power plants) in the utilization of fossil fuels (e.g., coal and petroleum products). The value added and innovative utilization of the flyash would support economic benefits and sus-

**Table 8.1** A summary of vanadium extraction process options

Process option	Description	Reference
Option #1	A hydrometallurgical conventional process involving concentrated H <sub>2</sub> SO <sub>4</sub> leaching of flyash followed precipitation and purification to produce V <sub>2</sub> O <sub>5</sub> as the product	US Patent 3,416,882 (Whigham 1968)
Option #2	A hydrometallurgical process that uses concentrated alkaline hydroxide leaching of flyash to recover vanadium selectively, followed by staged precipitation with lime, bicarbonate and CO <sub>2</sub> and CO <sub>2</sub> -ammonia to produce a calcined V <sub>2</sub> O <sub>5</sub> final product	US Patent 3,873,669 (Guillaud 1975)
Option #3	The carbonaceous feed material such as flyash is salt roasted at about 1000°C, leached with dilute alkali or water, followed by pure vanadium recovery as V <sub>2</sub> O <sub>5</sub> product (and other value metals if desired) by elegant precipitation and drying steps	US Patent 4,539,186 (Schemel et al. 1985)
Option #4	A novel process for vanadium and zeolitic products recovery from flyash involving a preconditioning water wetting step followed by carbon removal by flotation, and pressure leaching with dilute NaOH, and leach liquor treatment by solvent extraction and precipitation steps	US Patent 4,798,709 (Lakshmanan et al. 1989)
Option #5	A pyrometallurgical process involving reduction of metal oxides in flyash in a gas fired smelter at about 1550°C to produce a ferrovandium alloy as the final product	US Patent 5,685,244 (Goldfarb and Woodroffe 1997)

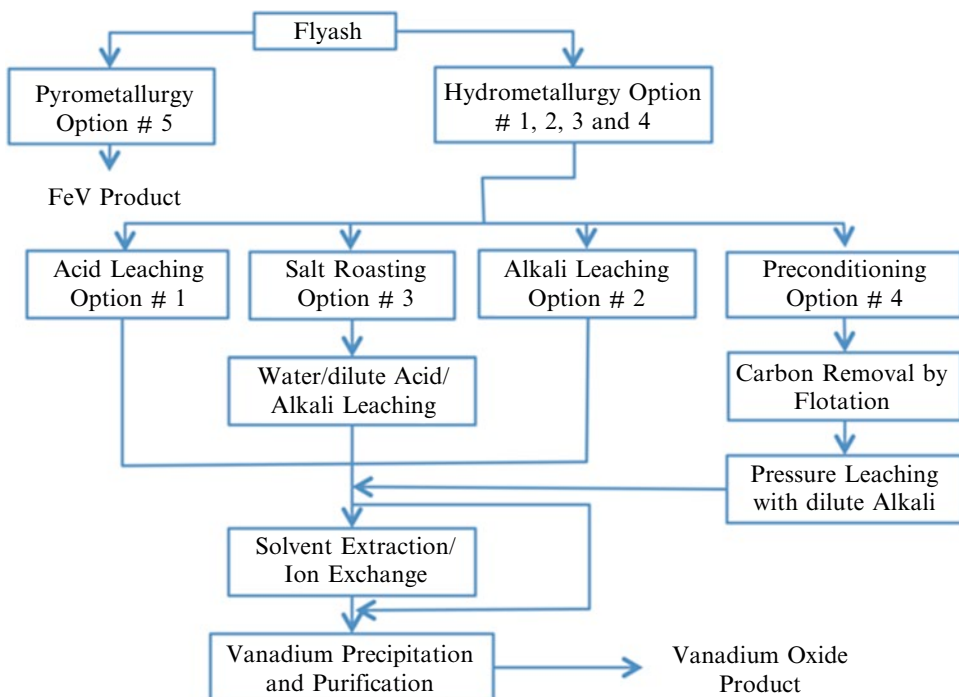
tainable environmental solutions (Singh and Gupta 2014). Flyash contains a large number of heavy metals and trace concentrations of specific heavy metals, and other substances that are known to be detrimental to health in sufficient quantities. Examples of such metals include arsenic, cadmium, chromium, molybdenum, selenium, thorium, uranium, vanadium, copper, zinc, and lead. These metal ions get released readily in aqueous environment, causing future threat to the environment. The unmanaged flyash may result in significant problems for the environment and ecology. Several utilization routes for flyash have been developed, considered for use, and some applied on large scale. Some of the application topics include (1) absorbent for cleaning sulfur compounds from flue gas; (2) adsorption of NO<sub>x</sub>; (3) removal of mercury and boron; (4) removal of phosphate and fluoride; (5) removal of phenolic compounds and gaseous organics; (5) production of bricks as building material; (6) soil amendments associated with agricultural, wasteland reclamation and forestry sectors; and (7) recovery of value added metals.

It is the metal recovery aspect of the flyash utilization, in particular vanadium recovery, that has been selected in this section to demonstrate the process selection methodology. Previously, separation processes for recovering ferrosilicon alloy (e.g., Pickles et al. 1999), chromium (VI) (e.g., Dasmahaputra et al. 1998), gallium (e.g., Fang and Geaser 1996), and vanadium, (and nickel and magnesium) (e.g., Kuniaki et al. 1998) were reported.

## 8.4 Vanadium Recovery from Flyash: Process Options

Several approaches for the recovery of vanadium from fly ash have been developed (e.g., Ye 2006). A simplified flowchart in Fig. 8.1 illustrates the approaches and the process options considered to demonstrate the process selection methodology.

A summary of the selected five process options are given in Table 8.1 and illustrated



**Fig. 8.1** A generalized flowchart of process options for vanadium extraction from flyash

through simplified process flowcharts in Figs. 8.2, 8.3, 8.4, 8.5, and 8.6.

The key performance aspects and associated performance measures are given in Table 8.2.

## 8.4.1 Description of Process Options

### 8.4.1.1 Process Option #1: Concentrated Sulfuric Acid Leaching

In Option #1 (Fig. 8.2), the flyash (or the vanadium concentrate) is leached with concentrated sulfuric acid (~98 %) to dissolve the vanadium and form a slurry. After settling/filtration, the vanadium in the clear solution is oxidized to its pentavalent state. The vanadium is precipitated with an agent such as ammonia and the hydrated precipitate is filtered, dried, fused, and formed into flakes. In this process, the leaching is carried out around 50°C and the oxidation and partial precipitation with ammonia are performed between 80 and 90°C in the pH range of 1.7–2.1.

The separated precipitate, red cake is dried around 315°C and then fused in a fusion furnace at about 1000 °C in an oxidizing atmosphere to produce  $V_2O_5$ . The final flaked product contains typically 98 wt% V as  $V_2O_5$ , 1 % Fe as  $Fe_2O_3$ , 0.2 % Ni as NiO, 0.1 % Ti as  $TiO_2$ , and acid-insoluble materials of about 0.6 %.

Another earlier patent (Vezina and Gow 1968) has discussed concentrated sulfuric acid leaching to produce impure  $V_2O_5$  and carbonate purification to produce ammonium metavanadate. A variation of the sulfuric acid leaching of flyash with precipitation using alkaline magnesium reagents ( $MgO$ ,  $Mg(OH)_2$ ,  $MgCO_3$ , or mixtures) followed by solvent extraction of the leach liquor and vanadium purification steps has been reported in a patent by Pitts (1978).

### 8.4.1.2 Process Option #2: Concentrated Caustic Soda Leaching

In this process option (Fig. 8.3), an alkaline leach is used which selectively leaches the vanadium leaving iron and silicates in the residue. The

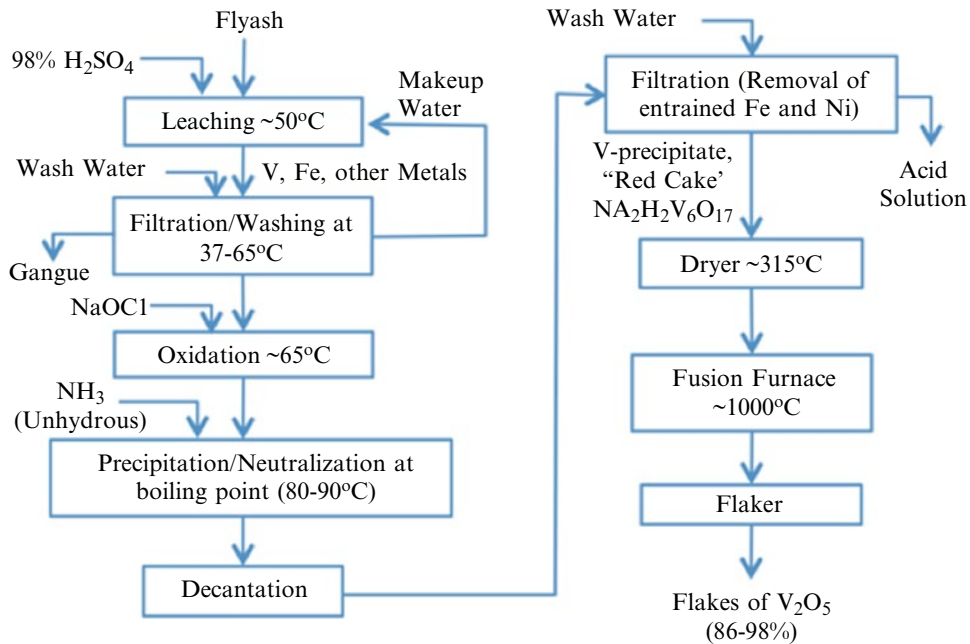


Fig. 8.2 Process flowsheet based on acid leaching of flyash (Whigham 1968)—Option #1

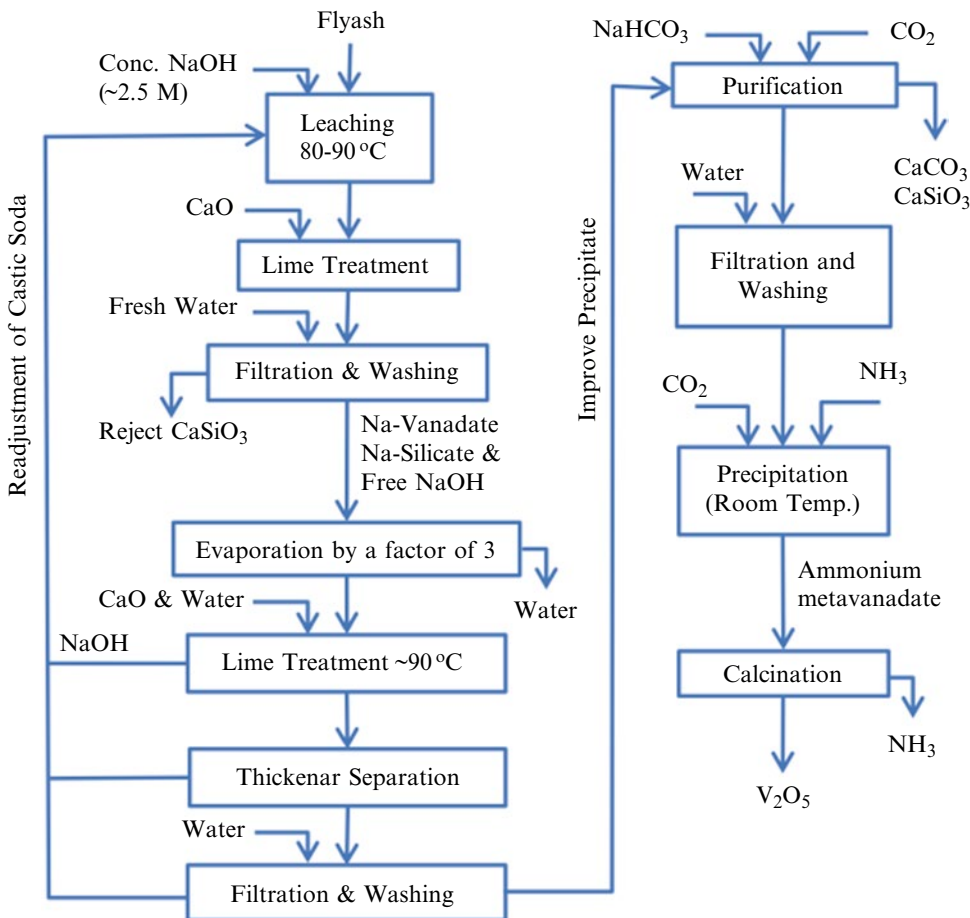
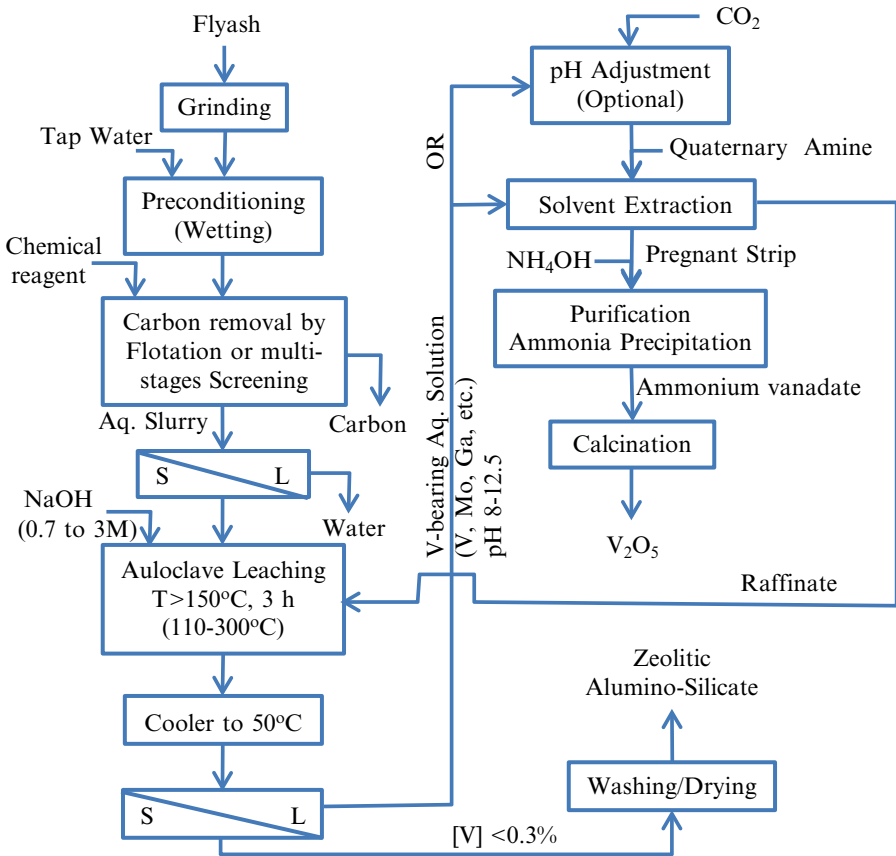
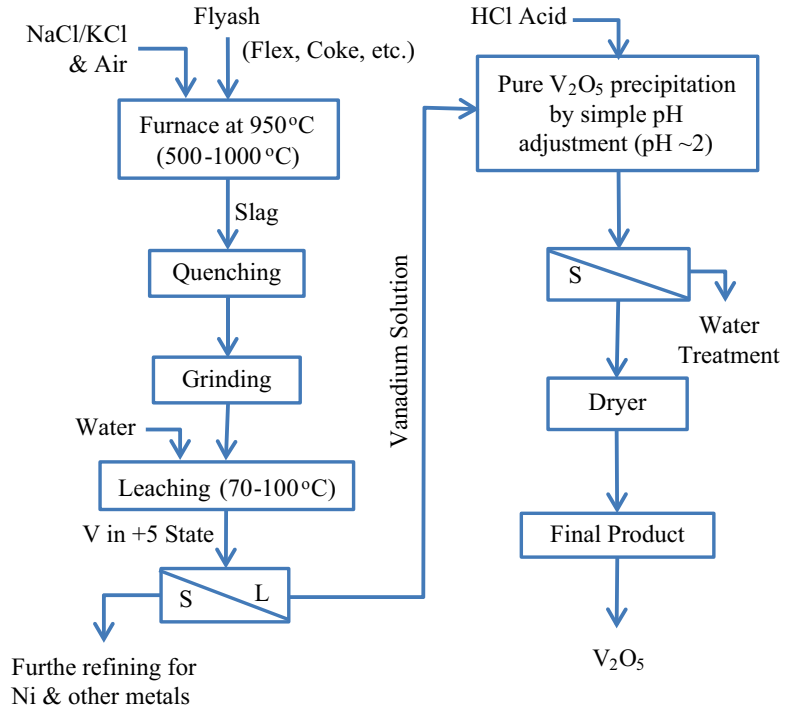


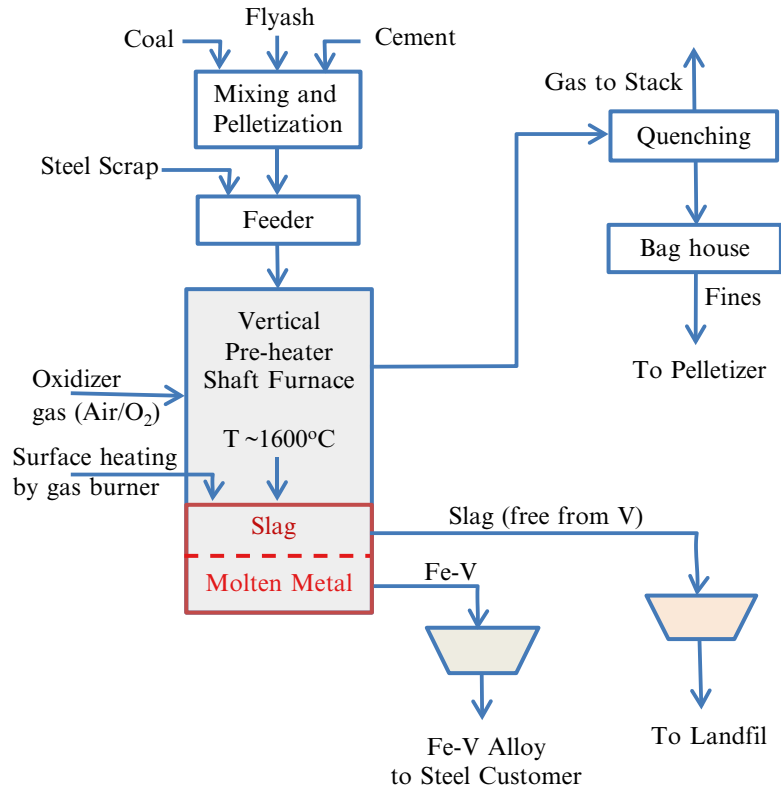
Fig. 8.3 Process flowsheet based on alkali leaching of flyash (Guillaud 1975)—Option #2

**Fig. 8.4** A process flowsheet based on salt roasting and water leaching of flyash (Schemel et al. 1985)—Option #3



**Fig. 8.5** Process flowsheet based on pre-conditioning and physical separation followed by alkali leaching of flyash (Lakshmanan et al. 1989)—Option #4

**Fig. 8.6** Process flowsheet based on pyrometallurgical separation of vanadium from flyash (Goldfarb and Woodroffe 1997)—Option #5



process is suitable for flyash from different sources containing different amounts of free carbon and vanadium oxides. Here, the flyash undergoes selective leaching with concentrated sodium hydroxide (2–5 mol/L) in a temperature range of 80–90°C. The slurry containing  $V^{3+}$  (in solution) and calcium silicates and other solids is treated with CaO at near boiling temperature to soluble calcium vanadate ( $V_2O_5 \cdot 4CaO$ ) and insoluble calcium silicate, and free NaOH. The solids are washed and the mixture filtered. The filtered solids contain all alumina, Fe, Ti, C, Mg, and alkaline salts. The solution containing over 80 wt% V and less than 1 % soluble silicate is volume reduced approximately by a factor of 3 in an evaporator. Excess lime is added to the concentrated solution to precipitate vanadium and calcium silicate. The slurry containing the precipitates is subjected to thickening, filtration, and washing. The separated calcium vanadate and silicate precipitates are treated extensively to produce pure  $V_2O_5$  as the final product. The

NaOH filtrates separated from various process steps are combined and concentration adjusted and recycled as reagent for vanadium leaching.

The purification of the mixture of calcium vanadate and silicate precipitates is performed by suspending the solids in an aqueous solution of  $NaHCO_3$  and bubbling with  $CO_2$  gas. The precipitated  $CaCO_3$  and calcium silicate are rejected by filtration and washing. The filtrate containing vanadium is next reacted with ammonia and  $CO_2$  at room temperature to precipitate ammonium vanadate, which is decomposed in a subsequent step to release free  $NH_3$  and to produce pure  $V_2O_5$ . The filtrate containing NaOH and the  $NH_3$  released from heat decomposition are recycled. The process refers to a pretreatment step to eliminate free carbon from the flyash, if necessary to avoid issues related to carbon residue in the process operation, by light roasting or flotation methods.

A variation of the alkaline leaching coupled with a second-stage sulfuric acid leaching is



**Table 8.2** Key performance aspects and related measures for metallurgical process selection and evaluation

Performance aspect (PA)		Performance measure (PM)	
PA1	Technical		
PA1.1	Functionality/reliability	PA1.1-PM1	Key process and equipment performance
		PA1.1-PM2	Metal removal efficiency
		PA1.1-PM3	Process control and product quality
PA1.2	Technology maturity	PA1.2-PM1	Stage of process development
		PA1.2-PM2	Previous application of the process within the industry or other related industry
		PA1.2-PM3	Past experience
PA1.3	Design life	PA1.3-PM1	Life-time in years
PA1.4	Operational	PA1.4-PM1	Operator safety
		PA1.4-PM2	Operation monitoring, control and maintenance
		PA1.4-PM3	Waste management
PA2	Financial		
PA2.1	Payout period	PA2.1-PM1	Payback period in years
PA2.2	Life-cycle cost	PA2.2-PM2	Capital
		PA2.2-PM3	Operating (decommissioning and waste management)
PA3	Regulatory/health and safety		
PA3.1	Regulator acceptance	PA3.1-PM1	Environmental impact (human and nonhuman biota)
		PA3.1-PM2	Worker health and safety
		PA3.1-PM3	Ability for the process to meet more stringent regulatory requirements by changes to processing components/steps
PA4	Timelines		
PA4.1	Schedule	PA4.1-PM1	Process implementation for metal recovery
		PA4.1-PM2	Process plant refurbishment after the first design life
		PA4.1-PM3	Decommissioning after final design life

reported elsewhere for vanadium and molybdenum separation from flyash of heavy oil-fired power station (Stas et al. 2007; Stas et al. 2010).

#### 8.4.1.3 Process Option #3: Salt Roasting Followed by Dilute Alkali or Water Leaching

In the published literature there are two patents (Schemel et al. 1985; Griffin and Etsell 1987) and some technical articles (e.g., Long et al. 2014) describe variations of the process involving salt roasting of flyash followed by alkali leaching for vanadium recovery.

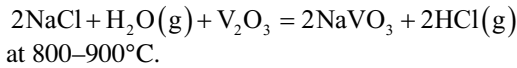
This process option (Fig. 8.4) provides a method for removing vanadium and other metals from carbonaceous vanadium bearing materials. The feed material is introduced to the furnace lined with fused alumina refractory and maintained in the range of 750–1000°C. Air is intro-

duced to the furnace at a rate controlled by the size of the furnace and the amount of carbon in the feedstock. The reaction results in the formation of a product which becomes a water-soluble salt. The product is quenched, and the slag is ground and subjected to leaching with water at a temperature of about 70–100°C. The water leaching brings vanadium in its pentavalent state to solution while other metals will be solids. After filtration and washing the solution is subjected to a unique precipitation step to form pure  $V_2O_5$  by simple adjustment of pH by the addition of an acid such as HCl. The precipitate is separated by filtration and washing, and sent for drying, followed by calcination in a furnace at about 950°C for several hours in the presence of air to produce the final  $V_2O_5$  product.

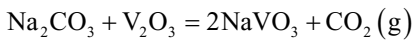
The objective of salt roasting is to render vanadium in water-soluble forms and is normally



carried out in a rotary kiln. General retention times are up to 10 h (Ye 2006). The temperature of roasting depends on the type of salt being used. For example, when NaCl is used, the following reaction occurs:



The salt roasting is generally the cheapest and attacks vanadium selectively. The soda ( $\text{Na}_2\text{CO}_3$ ) roasting is nonselective requiring relatively higher temperatures (900–1200°C) and is generally used to meet higher environmental requirements.



For roasting to be effective for vanadium oxidation, the process requirements are (1) free silica <3 %; (2) free lime <1 %; and (3) free oxygen >4 %. It should be noted that excess free lime produces insoluble metal vanadates and free silica forms a low melting oxide complex of Fe, Na, and Si ( $\text{Na}_2\text{O} \cdot \text{Fe}_2\text{O}_3 \cdot 4\text{SiO}_2$ ).

#### 8.4.1.4 Process Option #4: Preconditioning Followed by Carbon Removal and Pressure Leaching with Dilute NaOH

This process option (Fig. 8.5) allows the recovery of vanadium as  $\text{V}_2\text{O}_5$  and zeolitic aluminosilicates as final products from flyash and related carbon bearing, heat-treated materials. The process steps include (1) separation of carbon by water addition and multistage screening or flotation; (2) pressure leaching of the carbon-depleted flyash with dilute alkali metal hydroxide solutions at elevated temperatures; (3) recovery of vanadium from the leach liquor by solvent extraction, and as an option removal of other value metals present in the leach liquor; (4) precipitation of vanadium from the strip liquor in solvent extraction; (5) drying and calcination of the separated precipitate to produce pure  $\text{V}_2\text{O}_5$  as the final marketable product; and (6) treatment of the silicates in the leach residue separately to produce a zeolitic aluminosilicates as the second marketable

product, adding economic value to the overall vanadium recovery process.

The process chemistry and operating conditions for the key process steps are as follows. The free-carbon separation may be achieved by grinding the flyash and subjecting the particles to multistage screening using conventional equipment or flotation using conventional reagents and equipment (e.g., Aunsholt 1984). The pressure leaching of the flyash with a dilute alkali such as NaOH (0.7 mol/L) or up to 3 mol/L is carried out at temperatures between 100 and 300°C. The leach liquor with a solution pH in the range of 8–12.5 (preferably 8.3–10) is typically cooled to about 50°C and subjected to solvent extraction using a quaternary amine and an oxine in kerosene diluent. Any middle phase between the aqueous and organic phases in solvent extraction is prevented by the addition of a suitable amount of modifiers such as isodecanol. The loaded vanadium in the organic phase is stripped with a sulfuric acid solution. The strip liquor is precipitated with ammonia, filtered, dried, and calcined using conventional process steps. The separated leach residue is washed and dried.

#### 8.4.1.5 Process Option #5: Pyrometallurgical Process for Vanadium Recovery as Fe-V Alloy from Flyash

A pyrometallurgical process option is described in a patent by Goldfarb and Woodroffe (1997), and other variations of the process can also be found elsewhere (Ye 2006; Xiao et al. 2010). For Process Option #5 (Fig. 8.6), the patented process was chosen as the process. The process is a smelting-reduction process for reducing metal oxides, in particular vanadium oxides, present in oil and/or coal ash. The smelting furnace is fired by natural gas with oxygen or oxygen-enriched air. The molten metal layer is masked with a thick surface layer of slag to prevent re-oxidation of the metals.

This is a high-temperature process, which uses two heat sources to heat the ash, coal, and cement pellets fed to the furnace. The main source of energy is delivered by the top fired burners operating with natural gas or oil, and an oxidizer gas

(air/oxygen). The secondary source of energy is derived from the combustion of carbon present in the ash or coal. Metal oxides in the mixture (oxides of V, Fe) are reduced to molten metals by the carbon in the slag layer and by other optional, stronger reducing agents such as aluminum. The molten metal gravitates to the bottom layer in the furnace. The overlying slag layer shields the molten metal against oxidation by the oxidation atmosphere of the furnace and the burner jets. The surface temperature of the slag layer is maintained at about 1600°C. The slag constitutes up to 90 wt% of molten materials. The slag layer (about 7–12 cm thick), free of vanadium, is withdrawn, quenched and packaged for landfill disposal. The off gas is cooled with water heat exchangers. The carry-over particulates in the cooled gases are separated in the hot bag house and recirculated in the pelletizer. The molten metal layer is tapped by tilting the smelter. The tapped ferrovanadium, Fe-V, alloy is quenched and packaged in drums as product to steel customers.

The pyrometallurgical process is an environmentally friendly process. The slag generated as waste being a stable monolith, free of vanadium, can be readily disposed of without adverse effects to possible water leaching in the landfill sites.

The use of natural gas in the furnace instead of electrical energy (conventionally used) has been claimed to reduce significantly the cost of Fe-V production.

## 8.5 Process Option Analysis

General Considerations:

- The main marketable products from vanadium recovery are Ferrovanadium (Fe-V) alloy and vanadium pentoxide ( $V_2O_5$ ). It is assumed that both products have comparable market demand.
- Hydrometallurgical processes for vanadium recovery from flyash are considered attractive due to the relatively lower operating (energy) costs (Mambote et al. 2008).
- The pyrometallurgical process for flyash treatment is an environmentally friendly process.

The slag being a stable monolith, free of vanadium, can be readily disposed without adverse effects to possible water leaching in the landfill sites.

- It is important to recognize that the design of a low cost process for value-added product making with attributes such as closed-loop processing, which eliminates any harmful environmental footprints, would be an essential approach for the selection of the best process option for implementation.
- Alkaline leaching of flyash allows the treatment of silicates in the leach residue separately to produce a zeolitic alumino-silicates as the second marketable product, adding economic value to the overall vanadium recovery process.
- The processes selected are capable of producing marketable vanadium products such as regular grade FeV alloy 75–85 % V with high Al (1.5 % max) of low Al (0.5 % max), technical grade  $V_2O_5$  (83–86 % pure), fused black oxide  $V_2O_5$  (86–92 % purity), or 98–99 % or greater purity  $V_2O_5$ , depending on the purification route.

### 8.5.1 Assumptions and Scoring Scale for Performance Aspects

#### 8.5.1.1 PA1: Technical

##### PA1.1: Functionality/Reliability

The performance measures selected for this performance aspect are (1) key process/equipment performance, (2) metal removal efficiency, and (3) process control and product quality.

The characteristics of acid leaching in Option #1 include (1) high acid consumption, (2) a requirement for acid-resistant equipment, (3) treatment of acidic wastewater effluent, (4) treatment of solid residues before discharge (Long et al. 2014), and (5) nearly all metals present in the source material are leached with vanadium, which would require extensive purification of the solution generated in the process downstream in order to obtain high purity vanadium pentoxide (Lakshmanan et al. 1989).

Alkaline leaching used in Option #2 results in (Long et al. 2014) (1) reduced impurities in the leach solution that is beneficial for subsequent processing, (2) low requirement for corrosion-resistant equipment, and (3) direct discharge of water and solid residues after simple treatment. High concentration alkaline leaching of flyash can recover about 84 % vanadium (Chmielewski et al. 1997). However, the residual ash would be left with about 15 % nickel, which may not be

environmentally friendly as such metals can dissolve in water and reach the food chain.

Roasting of the source material such as flyash with sodium salts (e.g., NaCl) is generally preferred for high vanadium content ash. The chemistry can be complicated as a narrow temperature control would be necessary (Guillaud 1975).

The scores assigned to performance aspect, PA1.1, for Process Options #1–#5 are “1, 9, 4, 9, and 9,” respectively (Table 8.3).

**Table 8.3** Performance aspects and measures with scoring, weighting, and ranking for each vanadium recovery option from flyash

Performance aspect	Performance measure	Process options				
		#1	#2	#3	#4	#5
PA1—Technical						
PA1.1—Functionality/reliability	– Key process and equipment performance	1	9	4	9	9
	– Metal removal efficiency					
	– Process control and product quality					
PA1.2—Technology maturity	– Stage of process development	9	9	9	9	9
	– Previous application of the process within the industry or other related industry					
	– Past experience					
PA1.3—Design life	– Lifetime in years	4	9	4	9	4
PA1.4—Operational	– Operator safety	1	9	4	4	4
	– Operation monitoring, control and maintenance					
	– Waste management					
PA2—Finance						
PA2.1—Payout period	– Payback period in years	4	9	4	9	9
PA2.2—Life-cycle cost	– Capital	1	4	4	4	9
	– Operating (decommissioning and waste management)					
PA3—Regulatory/health						
PA3.1—Regulator acceptance	– Environmental Impact (human and nonhuman biota)	4	4	4	9	9
	– Worker health and safety					
	– Ability for the process to meet more stringent regulatory requirements by changes to processing components/steps					
PA4—Timelines						
PA4.1—Schedule	– Process implementation for metal recovery	4	4	4	4	9
	– Process plant refurbishment after the first design life					
	– Decommissioning after final design life					
Weighted score (equal weight <sup>a</sup> )		3.6	5.9	4.3	6.8	8.4
Ranking		5	3	4	2	1
Weighted score (unequal weight <sup>b</sup> )		3.7	6.4	4.5	7.9	8.0
Ranking		5	3	4	2	1

Notes: <sup>a</sup>Equal weighting of performance aspects (2.5, 2.5, 2.5, 2.5, respectively)

<sup>b</sup>unequal weighting of performance aspects (4, 1.5, 4, 0.5, respectively)

### PA1.2: Technology Maturity

Technology maturity of the process options is to be judged and scored by considering key measures that include (1) stage of process development; (2) previous application of the process within the industry or other related industry; and (3) past experience with the process. In the present evaluation, the chemistry, operation, and equipment of all processes have been used in the industry in one form or the other for metal extractions from source minerals or waste materials. Some plant applications of the processes have occurred in the past for vanadium extraction from waste materials including from flyash. However, it appears that there are no plants producing vanadium from flyash. The assumption here is that all process options are well developed and are available for deployment when necessary. Thus, a score of “9” has been assigned to all five options.

### PA1.3: Design Life

The single performance measure for the design life is lifetime in years. The design life of the hydrometallurgical process plants are expected to be relatively greater than the pyrometallurgical process plants. Thus, a high score of 9 is assigned to Process Options #2 and 4, and a score of “4” to Option #5. Similarly, for process complexity reasons, Options #1 and 3 are given each a score of “4”.

### PA1.4: Operational

Operator safety, and operation monitoring, control and maintenance are important performance measures. It is assumed that all process options have many common safety aspects built within the design and operating procedures. Aspects requiring more attention would be preventative maintenance and control and adequate operator training of autoclaves used for pressure leaching in Option #4, high-temperature salt roasting equipment in Option #3 and maintenance and control related to smelter/furnace, and flu gas treatment system in Option #5. The relatively large footprint of concentrated  $H_2SO_4$  leaching plant (Option #1) is given a low score of “1” for operational aspect, for reasons of (1) large vol-

ume reagent usage, (2) relatively larger volume process and effluent stream handling with dissolved toxic metals present, and (3) corrosion issues associated with equipment and components in the process.

The solvent extraction or ion-exchange processing steps used in vanadium recovery from leach solutions, for example, in Options #1 and #4, can result in operational control issues due to third phase formation in solvent extraction operation, and hence loss of efficiency, and similarly a limitation on the availability of selective and high loading capacity resins in ion exchange.

Additional operational complexities of treating off gases from Options #3 and #5 and pressure leaching equipment in Option #4 have resulted in a medium score of “4” being assigned to each of these options (see Table 8.3).

The scores assigned to operational aspect, PA1.4, are “1, 9, 4, 4, and 4” for Process Options #1–#5, respectively (Table 8.3). A high score of “9” for Process Option #2 is mainly to reflect the attractive performance measures related to safety, maintenance and control and waste management.

### 8.5.1.2 PA2: Financial

The key performance measures are (1) payback period in years, (2) capital cost, and (3) operating costs that include the standard process plant operating cost plus the cost collected now for future decommissioning and waste management.

#### PA2.1: Payout Period

The payback period is defined as the time to recover the capital investment associated with the implementation of the process option. A relative score of 1 or 9 is assigned for payout period if the time is greater than or less than, respectively, the target payback period of 5 years.

#### PA2.2: Life-Cycle Cost

Life-cycle cost is an important factor that accounts for capital, operating, and all other costs such as waste management, plant refurbishment, and decommissioning. Determination of the life-cycle cost at the Stage 1 evaluation would be beneficial in the selection of the preferred option.

If sufficient data are not available to perform this cost calculation, it must be definitely done prior to detailed plant design in Stage 2 evaluation. The Option #1 is scored low (“1”) on the basis of anticipated high cost of maintenance, high reagent cost (as nonselective reaction between  $\text{H}_2\text{SO}_4$  and all metal oxides in the flyash), effluent management, equipment corrosion issues, and negative environmental impacts due to nonselective removal of toxic and other metals present in the flyash.

The Option #5 is given a high score of “9” because of the simplicity of equipment and processing steps, and relatively lower operating and waste disposal costs. Considering the attributes for low and high scores for Options #1 and #5, Options #2, #3, and #4 are assigned a medium score of “4”

### 8.5.1.3 PA3: Regulator/Health and Safety

#### PA3.1: Regulator Acceptance

The success of a process to meet regulatory acceptance may be evaluated as measured by environmental impact (human and nonhuman biota), worker health and safety, and ability for the process to meet more stringent regulatory requirements by changes to processing components/steps.

Handling of  $\text{V}_2\text{O}_5$  in plant operation and loss of material to the environment can have negative impacts on humans and animals. Vanadium as  $\text{V}_2\text{O}_5$  (CAS No. 1314-62-1) has been classified by IARC (IARC 2006) as possibly carcinogenic in humans, with inadequate evidence of carcinogenicity in humans and sufficient evidence in animals. In a study, inhalation exposure has resulted in increased incidence of alveolar/bronchiolar neoplasms in mice and male rats but no human carcinogenicity data has been reported.  $\text{V}_2\text{O}_5$  is a respiratory irritant and at high doses can cause “boilermaker’s bronchitis.” Workers exposed to 0.1–0.3  $\text{mg}/\text{m}^3$   $\text{V}_2\text{O}_5$  for about 6 months have reported symptoms of ear, nose, and throat (ENT) irritations and exhibited signs of pharyngeal infection, etc. (OEHA 1999).

Ferrovandium, Fe-V, (CAS No. 12604-58-9) is a noncombustible solid but the dusts from the alloy can form explosive mixtures in air presenting fire and explosion hazard when exposed to heat or flame. The dust from Fe-V can be found in various sizes and it can enter the environment through industrial discharges or spills. Fe-V produces toxic vanadium oxide gas on combustion. It can react violently with strong oxidizers like chlorine (Vincoli 1997). Fe-V is generally stored at low temperature away from oxidizing agents. Health effects include irritation of ENT and affected organs are respiratory system and eyes. Exposure limits in general industry is 1  $\text{mg}/\text{m}^3$ .

Thus, with regard to health and environmental aspects, Fe-V may be considered to be relatively superior to  $\text{V}_2\text{O}_5$ , but for this analysis both Fe-V and  $\text{V}_2\text{O}_5$  products are assigned a medium score “4”.

Chloride salt roasting (Option #3) can cause serious environmental pollution with relatively toxic gases and waster. In this context, the concentrated  $\text{H}_2\text{SO}_4$  (Option 1) or high concentrations of caustic soda used in alkali leaching (Option #2) can produce large volumes of solid and liquid effluents, requiring comprehensive effluent management. As a result, a score of “4” has been assigned to Options #1, #2, and #3. The simplicity of processing steps that include the use of relatively less severe chemicals and low effluent generation in Options #4 and #5 has allowed a high score of “9”. The details are summarized as follows.

It is expected that the regulator would view several characteristics of the selected process options favorably. However, certain features would be also looked upon not so favorably. For example:

- Option #1 nonselectively dissolves most metal oxides from flyash into solution, creating toxicity issues with regard to liquid effluent discharges. The solid residues require extensive treatments for safe management. Corrosion and spills related too large amounts of concentrated sulfuric acid would pose additional focus on safety of operating staff.

- Option #2 has some selectivity for vanadium leaching and use of caustic soda results in less corrosion and other operator safety issues. Proper treatment of the solid residue free of vanadium allows the production of another marketable product, a zeolitic material, which would minimize the amount of effluents to be managed. However, this aspect is not included in this process option.
- Option #3 involves oxidative roasting of the ash containing free carbon or no carbon at high temperatures, which can emit toxic gases requiring proper off gas treatment. But the leaching of the residue with water or dilute alkali ensures removal of vanadium easily. Equipment control and adequate maintenance are essential components of the reliability of the process.
- Option #4 has a room temperature physical separation step to remove free carbon, if present, and employs pressure leaching at moderate temperatures with dilute alkali. The use of established autoclave technology allows efficient extraction of vanadium. The marketable zeolitic alumino-silicates by-product produced by a simple physical treatment is an added feature that reduces environmental discharges and can offer favorable economics.
- Option #5 is considered to be a favorable process in most performance aspects except design life and operational aspects. The less number of processing steps and a small footprint for easy construction and decommissioning make this option very attractive. Effluent generation is insignificant and the stable slag produced in the furnace can be readily disposed of in landfills.

For reasons discussed above, the performance aspect of regulator acceptance is given a score of “4” with regard to Options #1, 2, and 3, and a “9” for Options #4 and #5.

#### 8.5.1.4 PA4: Timelines

The schedule/timelines for (1) process implementation for metal recovery, (2) process plant refurbishment after the first design life, and (3) decommissioning after final design life are key

measures that can have a significant impact on obtaining regulatory approvals, firming up financing arrangements and keeping costs under control. The relative differences for these factors among the various process options can also determine in concert with other performance aspects the selection of the preferred process. In the absence of adequate data to support differences among the five options, a score of “4” has been assigned to all five process options.

### 8.5.2 Overall Analysis: Ranking of Process Option

The scores are summarized in Table 8.3. If the weights are assigned to the performance aspects, then overall scores can be deduced to arrive at a ranking of the options. If equal weights are adopted for the main four performance aspects (2.5, 2.5, 2.5, 2.5), as shown in the bottom part of the table, Option #4, (a hydrometallurgical process involving a physical carbon removal step followed by pressure leaching with dilute alkali for extraction, and solvent extraction, precipitation and calcination for the purification of  $V_2O_5$ ) and Option #5 (comprising a pyrometallurgical process to produce FeV as the final product) rank high compared to other process options. To assess the sensitivity of weighting on the performance factors, an arbitrary unequal weighting of the four performance aspects (4, 1.5, 4, 0.5) was chosen. If unequal weights are used and the technical and regulatory aspects are given significantly more importance (“4” each) than other performance aspects with finance as the second most important aspect, then again Options #4 and #5 appear to surface as the most attractive options.

The advantage of the proposed methodology is that the impact on all key performance aspects for the different process options are all considered and supported as much as possible either conceptually or based on past experience (and quantified if adequate data are readily available) and assembled in a single table to enable the effect of weighting to be easily assessed. Also, the effect of a change in any one score on the overall ranking can be easily assessed. This has



the benefit of focusing actions to arrive at a short list of the best-preferred options. For example, if technical and life-cycle cost effects can be favorably brought to Options #4 and #5 through innovative developments, even Option #1 could jump to the short list of best options for detailed evaluations in Stage 2 analysis.

Thus, based on assigned weights and estimated scores for the impact on performance aspects, the Process Options #4 and #5 can be short-listed for consideration in the second-stage analysis.

## 8.6 Path Forward: Next Stage 2 Process Selection Analysis and Implementation

The short-listed options from the first-stage analysis will have to be further evaluated through a detailed calculation of the impacts to arrive at the best process option.

In the second-stage analysis, quantitative information for the various performance factors will be obtained for each of the short-listed process options. For example, sufficiently detailed analysis of the following items will be made. They include (1) performance data for the short-listed processes by tests at a suitable scale to obtain and verify design and operating information, (2) a detailed evaluation of the applicable environmental regulations and its impacts, (3) design of the short-listed process plants, and (4) estimation of the capital and operating costs of the plants including the life-cycle costs. The detailed data will be used to develop appropriate scoring scales for each of the performance measures.

The methodology used for the Stage 1 analysis will be repeated with the new data for the short-listed options. A parametric sensitivity analysis of all performance factors (performance measures and performance aspects) will be carried out with the revised scores in an iterative manner, as necessary.

At this stage, other performance factors should also be considered prior to taking the final deci-

sion for the implementation of the selected best process option. The other performance factors may include:

- Capital availability and return on investment tolerances
- Market process swings for the products produced by the selected process
- Market size ranking
- Emerging regulatory and sustainability issues

Some of the above aspects including technology maturity have been discussed recently (King 2014) in conjunction with a retrospective SWOT analysis for new processes for metal production. In addition, certain nontechnical questions that may be asked and accountable in the project implementation (King 2014) may include:

- Why are we doing the project? (Question at the project beginning and end)
- Is this a legacy project? (Determine if political or personal agenda overruling standard technical and engineering practices)
- Is the project repeating history? (Substantiate if the project is different from similar projects which have failed)

The results will be compared between the short-listed process options, and the best preferred process option will be selected for implementation. It should be noted that the Stage 2 evaluation will require considerable efforts involving process plant design, cost estimation, and impact analysis pertaining to health, safety, and environment. Evidently, there is sufficient incentive to select a minimum number (e.g., 2 or 3) of the short-listed options from Stage 1 analysis. It is for this reason that adequate considerations of all available process options and performance factors should be identified and analyzed without bias or a priori judgement in the Stage 1 evaluation.

As stated earlier in Sect. 8.2, a detailed Stage 2 evaluation and demonstration of the methodology is beyond the scope of the current objectives and will not be pursued further.



## 8.7 Summary

- A structured first-stage evaluation of five process options for the recovery of vanadium from flyash as the source material to produce a marketable quality product, Fe-V or  $V_2O_5$ , was evaluated to select a short list of the preferred options. To achieve this goal a set of performance aspects and the related performance measures were used. On the basis of equal weighting factor for the different performance aspects, and scoring and ranking, two process options from among the five initial options considered were selected for the next-stage detailed analysis and to select the best option for implementation.
- If the weights for performance aspects are selected and fixed, a short list of options can be deduced for detailed evaluation of impacts on the performance aspects to arrive at the best option.
- The vanadium recovery example discussed to illustrate the process selection methodology should be viewed only as an exercise to illustrate the approach. The goal was not to recommend or endorse with special interests any one process.

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