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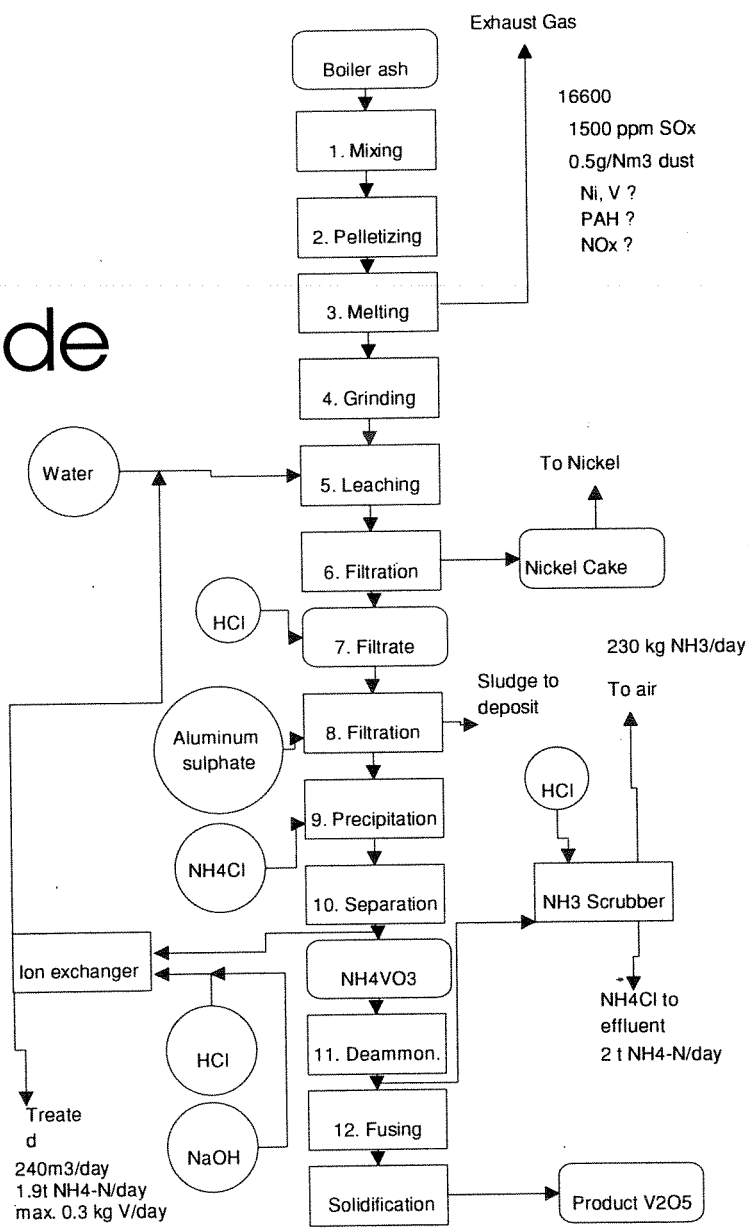
Estudio de Impacto Ambiental de projecto VNRP

Preliminary Environmental Impact Assessment for a plant for the recovery of vanadium and nickel from Flexicoke (VNRP) at Refineria de Amuay, Venezuela

2nd edition



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Estudio de Impacto Ambiental de projecto VNRP

Preliminary Environmental Impact Assessment for a plant for the recovery of vanadium and nickel from Flexicoke (VNRP) at Refineria de Amuay, Venezuela. (2nd edition).

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Abstract: This preliminary EIA is a preconseption of the Vanadium and Nickel Recovery Processes, which will eventually be realized to extract 7.2 tV as vanadium pentoxide and 1.3 t Ni as nickelsulfide per day from fly ash, produced in a rate of 25 t/d in the CFAY plant. The daily effluent flow rate from the Vanadium recovery process is estimated to 240 m^3, containing <200 mg TSP/l, <1 mg V/l and 16.2 g N/l, if untreated. The N- and V-content in the effluent may be reduced by recycling processes and different waste water treatment methods. The flue gas is estimated to contain 1500 ppm SO_x (4290 mg/m^3, emission rate 33g/s), and 500 mg TSP/Nm^3 (emission rate 2.3 g/s), provided baghouse treatment for particle reduction. The amounts of solid waste (sludge) from the vanadium recovery has not been quoted. The solid waste production of the nickel recovery process is estimated to 2 t/d. A landfill will have to be constructed to take care of the solid waste. Different mitigating actions are recommended to reduce gas emissions, effluent discharges, in particular the nitrogen content, and the production rates and contaminant contents of solid waste, to ensure that legal and environmental acceptable limits are kept.

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2.
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Estudio de Impacto Ambiental de projecto VNRP

Preliminary Environmental Impact Assessment for a plant for the recovery of vanadium and nickel from Flexicoke (VNRP) at Refineria de Amuay, Venezuela (2nd edition)

Preface

After the edition of the first version of this report, more detailed information has been presented by KOBELCO on the nickel recovery process. The new information, included in the present version, has caused changes in chapter 5.5, 5.4 and 7.1. Only insignificant changes will occur in the atmospheric and marine discharges. According to the new information, the total amount of solid waste from the nickel recovery process is reduced from 5 to 2 t/d. Except for the latter, no changes have been made in the consequence analyses or conclusions concerning the enviromental impacts.

This report presents a preliminary Environmental Impact Assessment (EIA) study for the proposed Vanadium and Nickel Recovery Plant at the Amuay Refinery situated in western Venezuela. The study is based on information presented in two preliminary feasibility studies made by the Japanese company KOBELCO, and additional information obtained during the work.

The preliminary EIA has been prepared on contract for the Venezuelan oil company, LAGOVEN S.A. The work started up in February 1995. We wish to thank Ing. Liberio E. Martin and Lic. Carlos Pimentel who have been the responsible for following up the work at LAGOVEN. We will also thank Ing. Hernan Trujillo of LAGOVEN for his contribution to the water treatment discussion.

The study was performed in co-operation between Norwegian Institute for Water Research (NIVA) and Norwegian Institute for Air Research (NILU).

At NIVA Mr. Torgeir Bakke has played a major part in the initiation and during the execution of the project. He has also contributed directly to the report. Mr. Eigil Rune Iversen has been responsible for the process studies included in the report, and Mrs. Aud Helland has contributed to the evaluation of soil and sea bottom contamination. Mr. Bjarne Sivertsen and Mrs. Tone Bekkestad of NILU have made the evaluation of the atmospheric impacts. Mr. Vilhelm Bjerknes of NIVA has been the project manager and editor of the EIA. NIVA's Venezuelan representative, Mr. Ghassan Dagher has been to valuable assistance with formal issues. Thanks to the EIA contributors and other persons at NIVA, NILU and LAGOVEN who have assisted during the study.

Bergen, Norway 18. august 1995.

Vilhelm Bjerknes
Project Manager

Contents:

Summary

This Preliminary Environmental Impact Assessment (PEIA) is a preconception of the Vanadium and Nickel Recovery Process (VNRP) of the Refinery of Amuay. The idea behind the VNRP project is the recovery of vanadium (as vanadium pentoxide, V_2O_5) and nickel (as nickel sulphide, NiS) from fly ash. This fly ash will be produced in a rate of 25 t/d, and is the waste product from the CFAY project, constituting the provisional end product of the oil refining process of the Amuay Refinery.

The operation of the VNRP plant will be linked to the CFAY operation. This preliminary EIA recommends the utilisation of the gas cleaning facilities (baghouse) and the stack of the CFAY unit to take care of the exhaust gases from the VNRP process. In addition there will be need for effluent treatment, especially to take care of the high N-contents of the effluent water, and a landfill for disposal of solid waste. It is doubtful whether the facilities or capacity necessary to fulfil the two last mentioned needs are available at the refinery today.

KOBELCO (1993, 1994) has performed two preliminary feasibility studies on the vanadium and nickel recovery, preparing the basis for this preliminary EIA. The objectives of the VNRP is to reduce health and environmental risks from handling, storing and eventually shipping the toxic flyash, and to create a new profitable operation at the refinery.

The three main recipients influenced by the VNRP project are the air, the ocean and the ground. Due to their different potential for dispersion, the areas of dispersion and influence will differ for each of them. The influence area has been defined for air emissions as the area within which 50 µg SO_2/m^3 can be expected during certain meteorological conditions, which means a distance of about 50 km downwind both in SW-ward and E-ward direction from the refinery.

The schedule for planning, preparation and construction of the V(N)RP plant (exclusive of the nickel recovery plant) has been estimated to a period of 2.5 years, starting in the beginning of 1995 and terminating in the end of 2nd quarter of 1997.

During the peak period of the construction phase the need of manpower will be approximately 200 persons. The operation phase will demand for 35 employees for the vanadium recovery and 5 additional operators for the nickel recovery operation. The operation regularity will follow that of the CFAY operation, estimated to 300 days per year.

The demands of fresh water for the Vanadium recovery plant is estimated to 240 t/d, and 22 t/d for the Nickel recovery plant. The land area required for the Vanadium Recovery Plant has been estimated to 5.300 m^2. The actual site of the operation will most probably be close to the CFAY unit, south of Block 29 of the Refinery area.

The contents of vanadium and nickel in the raw material (fly ash) has been analysed to 51.36 wt% and 4.28 wt% respectively on carbon free base. The carbon content of the ash is 38.4 wt% based on a coke combustion efficiency of 97%.

Vanadium recovery process

The vanadium recovery process will follow 11 main steps:

1. Sodium carbonate ($NaCO_3$) is mixed with the ash in an amount of three times the theoretical value for the formation of $NiCO_3$ and $NaVO_3$.

2. Pelletizing.

3. Melting process, process temperature supposed to be 900-1000°C. Conversion of the nickel and vanadium content into $NiCO_3$ and $NaVO_3$. The exhaust gases (mainly CO_2) are supposed to join the flue gas coming from the CFAY pant, and to be ventilated to the atmosphere through the CFAY stack.

4. Grinding.

5. Leaching by adding water. Alkaline conditions will ensure that $NiCO_3$ will not be dissolved.

6. Filtering and separating the nickel residue, also containing some iron, silicium and aluminium. This filtercake is delivered to the nickel recovery plant for the extraction of Ni.

7. pH-adjustment to pH=7 by adding HCl to the filtrate from step 6.

8. Addition of aluminium sulphate as a flocculant. Filtering off impurities as $Al_2(Si_3)_3$. Disposal of filter cake.

9. Addition of ammonium chloride to the vanadate solution. Precipitation of ammonium metavanadate (NH_4VO_3).

10. Separation of ammonium metavanadate. Ion exchanging of the water phase for the recovery of vanadate, which is returned into the process when regenerating the ion exchanger. The ion exchanged water constitutes the main effluent from the vanadium recovery plant, with a rate of 240 m^3/d containing 115 g/l of Na_2SO_4, 27 g/l of NaCl, 24 g/l of NH_4Cl, and <1 mg/l of vanadium.

11. Deammoniation by heating and fusing to produce vanadium pentoxide. The liberated NH_3 will be trapped in hydrochloric acid in a scrubber, and ammonium chloride is formed in an amount of 2 t/d. Recycling of ammonium chloride should be considered to minimise the nitrogen discharge.

Processing 25 tons of ash/day gives 7.2 t of vanadium per day, creating the following losses to the environment (if not treated):

- Aquatic discharges:

-Flow rate	: 240 m^3/d
-pH	: 5.8-8.6
-Suspended solids	: <200 mg/l
-Na_2SO_4	: 115 g/l
-NaCl	: 27 g/l
-NH_4-N	: 16.2 g/l (combined effluent from ion exchanger and scrubber)*
-V	:<1 mg/l

* The total load of nitrogen as NH_4 will make about 4 t N/d or 1200 t N/year.

- Solid waste:
  -Sludge, mostly aluminium hydoxide and silica. High content of vanadate in pore water. Amount not quoted.

- Gas emissions
  - -Flow rate : 27720 Nm^3/h
  - -Exit temperature : 158°C (431 K)
  - -SO_x : 1500 ppm (4290 mg/m^3)
  - -SO_x emission rate : 33.0 g/s
  - -TSP : 500 mg/Nm^3*
  - -TSP emission rate : 2.3 g/s*
  - -NH_3 : 230 kg/d**

* Provided 95% removal in baghouse

** 99% efficiency of scrubber

Nickel recovery process

The nickel recovery process will include the following steps:

1. Nickel leaching with sulphuric acid.
2. Sedimentation.
3. Counter current washing and thickening.
4. Neutralization.
5. Filtration. Gypsum formed and discharged.
6. Nickel sulphide formation and precipitation by injection of H_2S.
7. Filtration. Separation of solid NiS.
8. Neutralization and discharge of filtrate.

Processing 25 tons of ash/day gives a yield of 1.12 tons of NiS/day. The discharges from the nickel recovery process are summarised below:

- Aquatic discharges:
  - -Flow rate : 22 m^3/d
  - -pH : 5.8-8.6
  - -Suspended solids : 200 mg/l
  - -Sulphide (S^{2-})* : ?
  - -Vanadate** : ?

  * Excess from the precipitation of NiS

  ** From pore water in nickel filter cake

- Solid waste

  The process include 2 main suorces of solid waste:

- The CCD process will result in 1.79 t/d of solid waste, including 0.18 t SiO_2, 0.38 t Fe_2O_3, 0.53 t $NaVO_3$ and 0.10 t NiO.
- The neutralization process, using lime, will generate 0.21 t/d of gypsum ($CaSO_4 \cdot 2H_2O$).

Atmospheric emissions

To consider the future impact of atmospheric emissions from the VNRP plant, maximum ground level concentrations ($\mu g/m^3$) 1-1.5 km downwind from the VNRP site have been estimated for SO_2, TSP and V_2O_5 with respect to short term (1 h) average and long term (annual) average:

	Short term ($\mu g/m^3$)	Long term ($\mu g/m^3$)
SO_2	33.8	3.4
TSP	2.4	0.2
V_2O_5	1.2	0.1

The SO_2 contributions of the VNRP plant will be 3.5% of the State of Washington standards, less than 10% of the WHO air quality guideline values, and about 1% of the total current emissions from the Refinery of Amuay.

For vanadium the maximum 1h average ground level concentration from the VNRP emission is estimated to 1.2 $\mu g/m^3$. Summarising the ground level concentrations of the VNRP and the CFAY gives a short term ground level concentration of 7.4 $\mu g/m^3$, which corresponds to a 24 h average of 3.8 $\mu g/m^3$. This is above the air quality guideline given by WHO (1988), stating that ambient concentrations less than 1$\mu g/m^3$ (24 h) is not likely to give adverse health effects.

The maximum annual average concentration of SO_2, 3.4 $\mu g/m^3$, resulting from the VNRP plant, is located over the Bay of Amuay, approximately 1.8 km west of the refinery, and represents approximately 1% of the total SO_2 impact from the refinery today. The maximum annual ground level concentrations of SO_2, TSP and vanadium from the planned VNRP plant are well below recognised air quality guidelines and standards.

Noise

Noise level specifications for the units of the VNRP project has not been available for the preliminary EIA. Assuming the principle applied for the CFAY project (NIVA in prep.), that no unit shall generate more than 85 dBA (those above being sheltered), noise modelling shows insignificant contribution to the total noise level in the urban areas considered. Modelling also shows that the number of single sources producing 85 dBA each, should have to be increased with a factor of 100 to create discernible increases of the noise level.

Effluent water

The effluent water will have to go through extensive treatment to attain the legal limit of 10 mg N/l. A high degree of recycling is recommended for the ammonium chloride coming from the ion exchanger and from the deammoniation step in the vanadium recovery process. Recycling 70% of the ammonium will give a rest concentration of 500 mg N/l and a flow rate of 810 g N/min. With primary treatment in a sour water stripper the N-content may be reduced to 10% of these values, making the effluent suitable for further treatment in the TRAY treatment unit before discharge via the artificial lagoon and further on to the Bay.

It is expected that nutrients and other salts will mainly exist in solution, while nickel and vanadium residues will mainly be particulate. As a worst case it may be considered that the process water of the VNRP will contain 200 mg particulate material pr liter, which will be diluted in the total water discharge to the Bay, which is approximately 1.7 x 10^6 l/d. This effluent carries 340 kg of suspended solid matter for the dilution of 300 g of vanadium, which gives a vanadium concentration of 800 mg/kg

in settling particulate material in the Bay. This concentration is within the range of vanadium concentrations already existing in the sediments of the South Bay.

The scarce information about the nickel recovery process gives no possibilities for making a corresponding estimate of the nickel contamination.

Soil
There are three potential sources of soil contamination from the VNRP:

1. Spill of ash, chemicals and intermediate products.
2. Wet depositions from air emissions and drainage water.
3. Drainage water from the potential storage site for solid waste.

The deposition site should be constructed to avoid mobilisation of metal residues. The basis for estimating the magnitude of such mobilisation is not available.

Recommendations
A combination with the CFAY baghouse cleaning will primarily benefit dust reduction. If connected to CFAY Alternative 1 (including scrubber cleaning of flue gases), a SO_2 reduction of 97% will be obtained, reducing the VNRP stack emission contribution to 1g SO_2/s.

Recycling of ammonium chloride from the ion exchange process and from the ammonium stripper before the introduction of the effluent water to the TRAY plant is recommended to lower the N-content of the effluent water under the legal limit of 10 mg N/l. Sour water stripping to get rid of surplus ammonia may become necessary.

A washing process with water or weak Na_2CO_3 is recommended to take care of the vanadium content in the sludge from step 8 in the vanadium recovery process, and to reduce the vanadium content in the effluent water, and in the sludge from the TRAY water treatment plant.

Programs for surveillance and control should be developed during the first year of operation of the VNRP, and then integrated in the total Refinery monitoring program. The program should include source- and impact monitoring of air emissions, effluent water, noise and soil contamination from solid waste deposits.

From an environmental point of view, the most critical part of the VNRP is the high N-content of the effluent water. Water treatment to obtain an acceptable (legal) N- concentration (<10 mg/l) will make the VNRP environmentally acceptable. Gas cleaning including particle removal (CFAY baghouse) and SO_2 reduction (sea water scrubber) is also strongly recommended.

1. Introduction.

1.1. General background

Extraction of vanadium from fossil fuels, including vanadium-rich oil and coal, tars, bitumen, and asphaltites, is important in several countries. A number of oilfields have high vanadium content, with levels up to 600-700 g vanadium/kg. For this reason, vanadium is extracted from petroleum ash in some countries (e.g., Canada, Italy, USA).

During the first half of the 1980s, the global production of vanadium (as vanadium pentoxide, V_2O_5) ranged from 34 to 45 million kg. China, Finland, South Africa, the USA, and the USSR are the biggest producers.

Vanadium is mainly (75-85%) used in ferrous metallurgy as an ally additive in various types of steel. It's use in non-ferrous metals is important for the atomic energy industry, aircraft construction, and space technology. Vanadium is also widely used as a catalyst in the chemical industry, and in small amounts for a variety of other applications (WHO 1988).

1.2. The present project

The present PRELIMINARY ENVIRONMENTAL IMPACT ASSESSMENT (PEIA) is a preconception of the environmental issues of the Vanadium and Nickel Recovery Process (VNRP) of the Refinery of Amuay, situated in the municipality of Los Taques in the state of Falcon in Venezuela. The refinery, established in the 1950's by Esso Oil Corporation or Creole is presently operated by Lagoven S.A. The refinery area is located adjacent to the Bay of Amuay on the west coast of the Paraguana Peninsula, approximately 10 kilometres north of the town of Punto Fijo. The refinery covers an area of approximately 22 km^2. The site is depicted on Figure 1.1. a-b.

The climate of the area is semi-arid, the average temperature is 27^oC, the relative humidity is 76 percent, and the wind is typically (in 90 percent of the days in a year) from the east at 55 kilometres per hour.

The refinery processes approximately 500 000 barrels of medium crude oil a day. In 1982 it was upgraded by adding the flexicoker to convert high boiling petroleum fractions into light hydrocarbons such as liquid petroleum gas, naphtha and distillates. The gasification also produces a low BTU fuel gas and two types of coke fines, a bed coke and a denser caked coke.

In 1982 the flexicoker unit of the Amuay Refinery (FKAY) was started up to extract the liquid and gaseous contents of coke. Flexicoke as a waste product is coming from the FKAY unit, located in Block 29 in the refinery area. To utilise the rest energy of the flexicoke, a new process unit (CFAY) is under construction at Block 29 of the refinery. The combustion energy from burning flexicoke in the CFAY plant will be utilised to produce high pressure vapour for new projects of the refinery.

The daily production of flexicoke is approximately 355 tons. The solid material (fly ash) coming out of the CFAY process is estimated to 25 tons/d. High contents of vanadium and nickel makes this material suitable for the extraction of these valuable metals.

KOBELCO (1993, 1994) has performed two preliminary feasibility studies on the recovery of vanadium and nickel utilising fly ash from the CFAY project as raw material. The vanadium pentoxide

(V_2O_5) extraction process is relatively detailed described in these studies, while presentation of the nickel sulphide (NiS) recovery process is incomplete.

This preliminary EIA is based on data from KOBELCO's preliminary feasibility studies. Parallel to this preliminary EIA, prepared by NIVA, KOBELCO is preparing a detailed feasibility study (DFS) on the Vanadium/Nickel Recovery Project (VNRP).

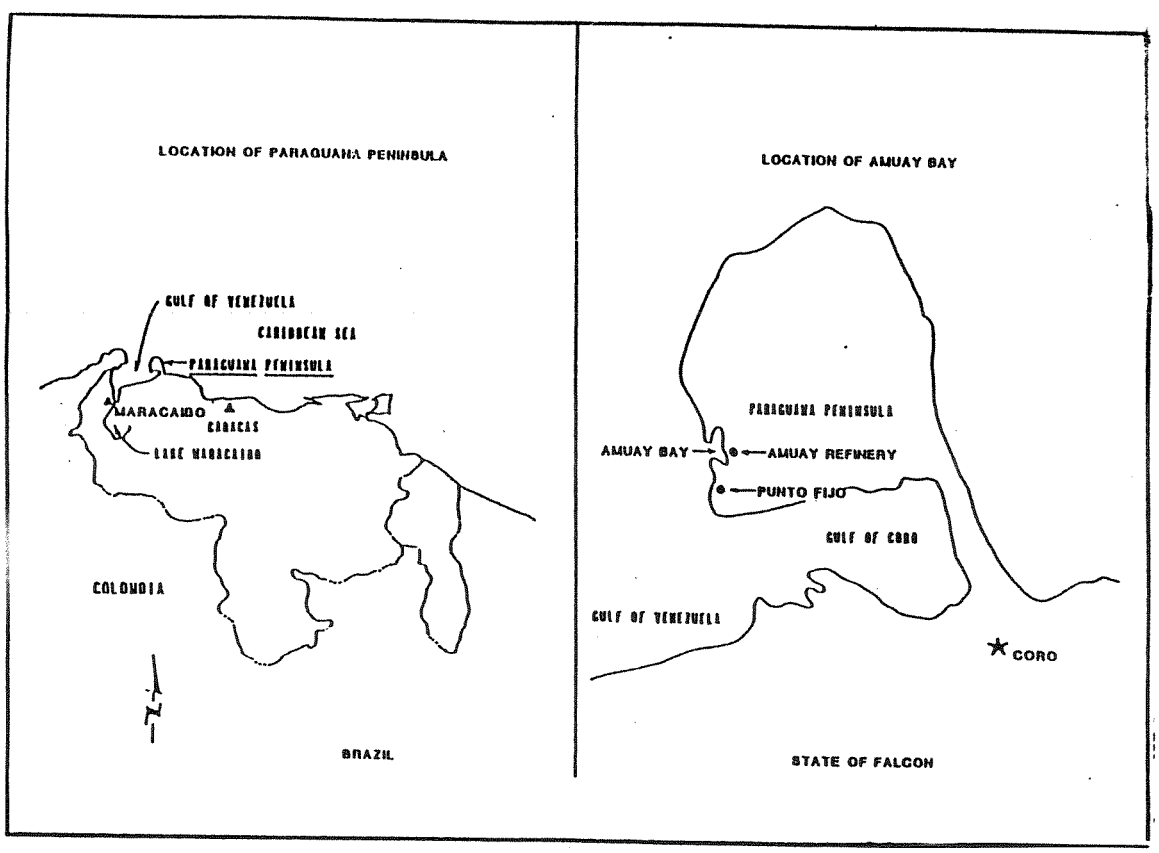


Figure 1.1.a-b. Map of Venezuela and Paraguana Peninsula, showing the location of the Amuay Refinery.

2. Objective and justification

2.1. Objective

The purposes of the VNRP are primarily to obtain environmental improvements by:

- Recovering vanadium and nickel from hazardous fly ash coming from the CFAY plant, and thereby prevent the environmental and legal disadvantages of storing and eventually shipping the fly ash.
- Reducing the amount and environmental risks of the terminal solid waste from the refinery.

The economical potential of the project, in terms of economic profit will be:

- The production of chemical compounds in great demand at the world marked.

2.2. Justification

The execution of the project allows for handling and safe consumption of the fly ash through which one will achieve:

- Prevention of problems arising from handling, transport and deposition or shipping of toxic fly ash vulnerable to diffuse emissions.
- Reduction of the volume of hazardous waste coming from the refinery processes.
- Commercial utilisation of chemical compounds extracted from hazardous waste material.
- Work and income for a number of hands.

2.3. The option of not executing the V/Ni Recovery Project

The prime consequence of this option is that daily produced fly ash will have to be handled, stored and eventually shipped as hazardous waste at the risk and responsibility of the Amuay Refinery. Secondly the option means wasted profit from the lost export of valuable chemical compounds.

3. Location and areas of influence

3.1. General principles of influence

The Amuay Refinery is located adjacent to the Bay of Amuay on the west coast of the Paraguana Peninsula, approximately 10 km from the town of Punto Fijo and 1 to 2 km from the town of Judibana. The Refinery covers an area of about 22 km^2. The Vanadium and Nickel recovery plant (VNRP) will be situated at Block 29, or close to Block 29 of the Refinery.

The three main recipients in the physical environment that can be influenced by the VNRP are the ground, the ocean and the air. The size of the influence area will differ for each of them. Airborne pollutants are transported and dispersed more rapidly than are pollutants in the ocean. Oceanic currents move much slower than wind. Thus also the dispersion of pollutants is slower. Transport of pollutants in the ground is a slow process, and the area of direct influence will be restricted compared to the ocean and the air.

In the CFAY EIA (NIVA in prep.) the influence area was defined from air emissions. This implied a distance of about 50 km downwind (50µg/m3 of SO2 was expected at this distance during certain meteorological conditions) both in SW-ward and E-ward direction. The north and southward radial distance were set to 5 km in each direction.

3.2. Areas of influence

3.2.1. Air

The town of Judibana is located only 2 km away from the refinery at what is normally the up-wind side of the refinery, which means that pollutants usually blow away from Judibana.

The total emissions of SO_2 from the refinery as of January 1995 is about 416 tonnes/day. Including the CFAY establishment and a DCAY regenerator without wet gas scrubber this yields a total emission of sulphur dioxide of approximately 440 tonnes/day or 5091 g/s. The total air pollution impact area resulting from the emissions covers at present distances of more than 50 km from the refinery. Downwind concentrations of SO_2 may during certain meteorological conditions reach 50 $\mu g/m^3$ at these distances. National and international air quality standards and guideline values are probably not exceeded beyond about 8 km from the refinery today. At closer distances from the refinery the highest one hour average concentration may exceed 1000 mg/m^3. The highest impact will normally be located west for the refinery area, on the Bay of Amuay and over the sea waters of the Gulf of Venezuela.

3.2.2. Ocean

Based on the modelling of discharge of cooling water to the Bay done in the CFAY EIA, it is assumed that the sea area potentially influenced by the VNRP outlet will be restricted to the Amuay Bay. The outlet of cooling water is approximately 1 km south of the VNRP outlet. Both the cooling water and the discharge from the VNRP runs into the surface water. The bay water has a retention time of 1.5 days (cf CFAY EIA).

3.2.3. Soil and ground water

The risk of contamination of the ground water and soil is either due to spill of ash and chemicals during the process, transport and shipping, leakage from disposed waste material, or airborne fall out of pollutants over a wider area. As the nickel and vanadium recovery process will take place under *"closed conditions"*, it is unlikely that the process itself will cause any contamination of the ground.

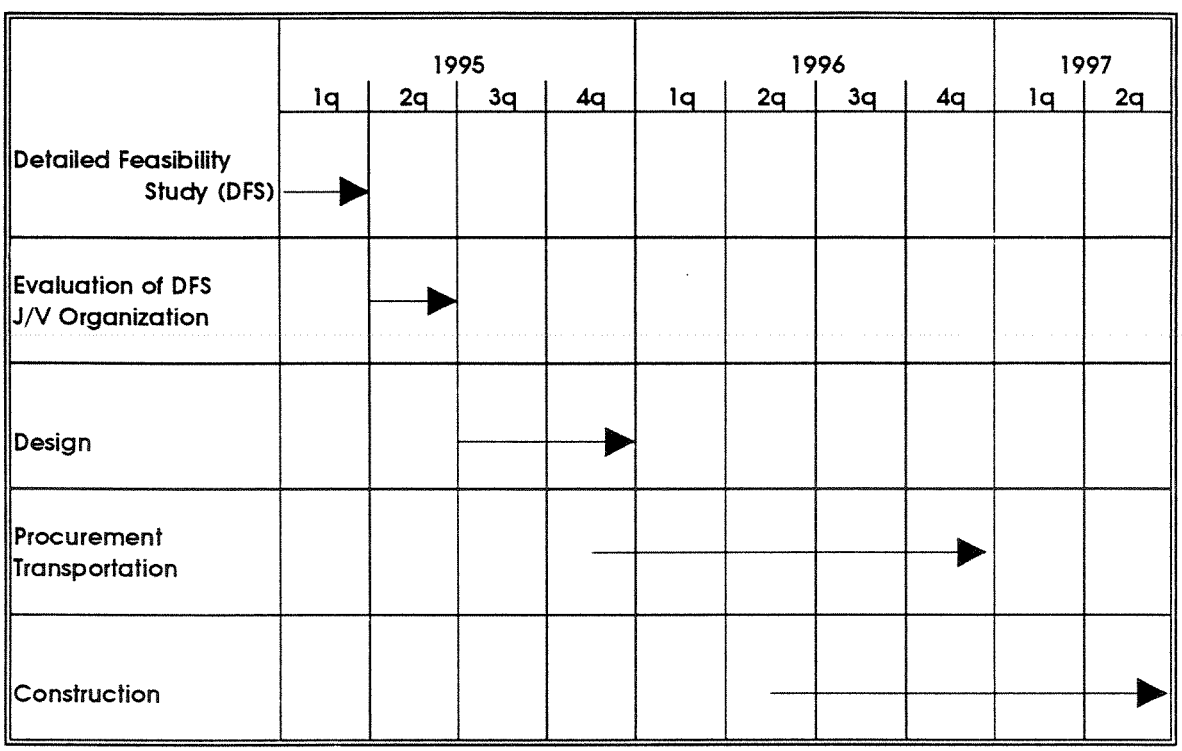
Depending on the process chosen, solid waste will be created from the nickel purification (5 tons/day if using lime as neutraliser or 1.2 tons/day if using spent caustic (NaOH) as neutraliser) and a sludge from the vanadium filtration (cf chapter 4). The deposition area for this waste is not known. The area of influence will be limited if modern precautions are followed, like using geotextiles before deposition, followed by capping and handling of the drainage water etc..

4. Time schedule, employment and services

4.1. Time schedule

The time schedule of the VNRP project is shown in Figure 6.1 below. The planning phase including a detailed feasibility study (DFS), project evaluation and joint venture organisation will take place during the first half of 1995. If decided, design, procurement and transportation of construction materials may start up during third and fourth quarter of 1995 and continue to the end of the year. According to the schedule construction of the plant may start up in the second quarter of 1996, and finish at the end of 1997.

Time schedule for the VNRP Project



This schedule does not include the nickel recovery plant, and it is uncertain whether this part of the project may be delayed or included later on.

4.2. Employment and services

The need for manpower for the construction phase is estimated to approximately 200 persons during the peak period.

The operation phase will demand for 35 employees, 9 for management, administration, inspection and analysis (daytime), 16 operators and 4 maintenance personnel. 6 daytime personnel are needed for the handling of raw material and products.

The figures presented here for the operation phase are based on a similar operation in Japan. There may be need for increasing the staff during the beginning of the operation. Incorporation of the Nickel

Recovery Plant will demand for 5 additional operators. This plant is considered to operate batch-wise in daytime only. The operation regularity is considered to be 300 days per year.

The supplies of fresh water required for the Vanadium Recovery Plant will be 240 t/d, and 30 t/d for the Nickel Recovery Plant. For supplies of chemicals, please see chapter 5 below. Figures for the requirements of electricity, fuel energy, steam, compressed air etc. are not yet ready, and will be presented in the DFS.

4.3. Area requirements

The required land area quoted by KOBELCO (1994) for the V_2O_5 Recovery Plant is divided in:

Plant Area	3.100 m^2
Storage Area	2.200 m^2
Total Area	5.300 m^2

It is still uncertain what will be the additional area requirements for the Nickel Recovery Plant.

5. Material Flow

5.1. Characterisation of raw material.

Analysis of the fly ash composition (carbon free base) has been performed for KOBELCO by TAIYO:

V_2O_5	51.36wt%
NiO	4.28 wt%
SiO_2	3.89 wt%
Al_2O_3	2.90 wt%
FeO_3	2.70 wt%
MgO	0.80 wt%
TiO_2	0.60 wt%
P_2O_5	0.30 wt%
Na_2O	<0.50 wt%
SO_3	32.46 wt %

The carbon content of the ash is 38.4 wt% based upon a coke combustion efficiency of 97%. Manganese and zinc has been detected, but arsenic (As) was not detected in the analysis. The bulk density of the feed ash is qouted to 0.50.

The plant capacity is based on the combustion of 355 t/d of flexicoke in the CFAY process, producing 25 t/d of ash being the raw material for the Vanadium Recovery plant. Recovery of V and Ni is performed in two separate processes, in two different plants, and with separate discharge effluents. Both projects are considered economically profitable. The regularity of the processes is estimated to 300 days per year, following the process rhythm of CFAY. The vanadium recovery plant will demand for approximately 240 t water/day. The water requirement of the nickel recovery plant will be approximately 22 t/d.

5.2. General description and material flow of the vanadium recovery process

The following is a presentation of the process, including rough estimates of the discharges. A block diagram of the process is presented in Figure 4.1.

In step 1 sodium carbonate (Na_2CO_3) is mixed with the ash. The required amount of sodium carbonate is three times as much as theoretical value (for the formation of $NiCO_3$ and $NaVO_3$). After pelletizing in step 2 (pellet size 5 mm), the mixture runs into the melting process in step 3. The operating temperature is not given, but we believe the process will run between 900-1000 ^oC. The melting point of sodium carbonate is 851 ^oC.

During the melting process the nickel and vanadium content in the ash will be converted into nickel carbonate and sodium vanadate. The process will produce exhaust gases (mostly CO_2), which will pass the CFAY baghouse and be mixed with flue gas from the CFAY plant before ventilation to the atmosphere through the CFAY stack.

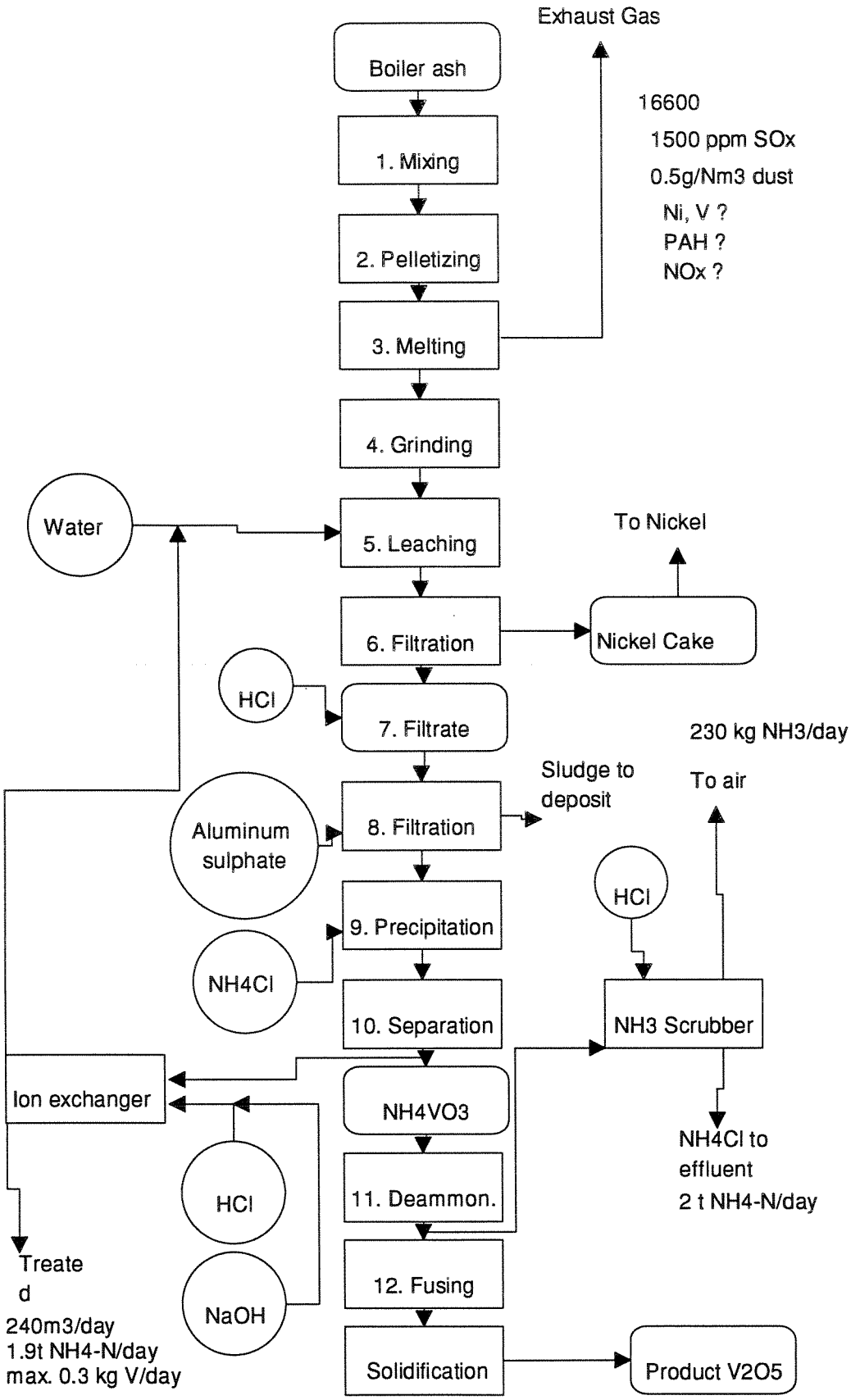


Figure 5.1. The vanadium recovery process. Flow chart.

After grinding in step 4 the smelted and grinded calcine is leached with water in step 5 to recover the vanadium as vanadate-ion. In the alkaline conditions the nickel carbonate will not be dissolved. The nickel residue will be filtered off in step 6. The filter cake, also containing some iron, silicium and aluminium, runs into the nickel recovery plant. Remaining Si will be precipitated as $Al_2(Si_3)_3$ during the 2nd filtration step.

The steps 7 and 8 are purification steps. The filtrate from step 6, containing the vanadate product is pH-adjusted with hydrochloric acid to obtain pH = 7. Aluminium sulphate is added as a flocculant and the impurities containing silica is filtered off as $Al_2(Si_3)_3$. According to KOBELCO the filter cake contains harmless substances, and no special precautions have been presented with regard to the disposal of the cake. The filter cake will however have a water content of about 70 % and the pore water will have the same vanadate concentration as in the filtrate. A collection of the seep from the filter cake pile should for this reason be considered and alternatively returned into the process (step 5).

In step 9 ammonium chloride is added to the pure vanadate solution, and ammonium metavanadate (NH_4VO_3) is precipitated . The precipitate is separated in step 10, and the water phase passes through an ion exchanger for recovery of vanadate. The vanadate is returned into the process when regenerating the ion exchanger. The ion exchanged water is directed into the sewage system of the refinery and constitutes the main effluent from the vanadium recovery plant.

The flow of treated water from the ion exchanger will have a rate of 240 m^3/d, containing :

Na_2SO_4	115 g/l
NaCl	27 g/l
NH_4Cl	24 g/l
V	<1 mg/l

In the next step (step 11) ammonia will be liberated from the ammonium metavanadate after heating and fusing and vanadium pentoxide is produced. The liberated NH_3 is trapped in hydrochloric acid in a scrubber, and ammonium chloride is formed. According to KOBELCO's process description the ammonium chloride will be discharged into the sewage system.

Discharge of vanadium to the treated water will be < 1 ppm. The slurry water from the nickel recovery part will have a pH within 5.8-8.6, and a content of suspended solids < 200 ppm.

According to KOBELCO, chloride will stay in solution during the precipitation of ammonium metavanadiate, and will leave the process during the filtration operation, and will thus disappear (via the ion exchanger) before the deammoniation step (step 11).

Recycling of the ammonium chloride should be considered to minimise the nitrogen discharge. Some NH_3 will however pass the scrubber into the atmosphere. We estimate the scrubber efficiency to 99 %. Since ammonia is completely neutralised, the ammonia concentration in the gas leaving the scrubber will be far below the permissible level.

5.2.1. Gas emissions from the vanadium plant

The following gas emissions will take place from the vanadium plant:

a) Exhaust gases from the melting process (step 3):

SO_X	: 1500 ppm
SO_x emission rate	: 2.3 g/s
TSP	: 500 mg/Nm^3
Flow rate	: 27720 m^3/h
Temperature	: 158 ^oC

b) NH_3 from the deammoniation process (step 11):

The NH_3 load on the scrubber is considered to be 2,3 tons NH_3/day. The efficiency of the scrubber will probably be high. A worst case efficiency estimate of 99 %, means an atmospheric discharge of 230 kg NH_3/day.

c) Building ventilation:

Data on discharge to the atmosphere have not been available.

5.2.2. Aquatic discharges from the vanadium plant

According to KOBELCO's description there will be two main water effluent flows leaving the vanadium recovery process:

- Treated water from the ion exchanger (step 10)
- Neutralised water from the deammoniation process (step 11)

Discharge from ion exchanger
KOBELCO has quoted the following discharge data for the ion exchange process (step 10):

Flow rate	: 240 m^3/day
Operation	: 300 days/year
pH in effluent	: 5,8-8,6
Suspended solids	: <200 ppm
Na_2SO_4	: 115 g/l
NaCl	: 27 g/l
NH_4Cl	: 24 g/l
V	: < 1 ppm

If not treated this will result in the following loads to the recipient :

NH_4-N	: 1,9 tons N/day or 564 tons N/year
V	: < 0,3 kg V/day or < 90 kg/year. Worst case 0,3 kg
V/day	

Discharge from deammoniation process
In the deammoniation process the liberated NH_3 is taken up by HCl in a scrubber. The neutralised ammonia (NH_4Cl) is discharged. From the vanadium content of the ash it is possible to calculate the load of NH_4Cl to the environment.

Processing 25 tons ash/day gives 7,2 tons V/day or 14 tons VO_3^-/day. This equalises 2,5 tons NH_4/day or 2 tons N/day.

The total load of nitrogen as NH_4 will make about 4 tons N/day or 1200 tons N/year, including the ammonia leaving the ion exchanger. Technically it is possible to recover the ammonia and recycle most of the ammonium chloride used in the process, but this possibility is not discussed in KOBELCO's process description.

5.2.3. Hazardous waste

The sludge from step 8, mostly aluminium hydroxide and silica will also contain pore water with a high content of vanadate. KOBELCO proposes the filter cake to be disposed in a landfill. At this stage it is impossible to estimate the loss of vanadium from the filter cake. It will however be possible to reduce this loss, and the subsequent ground water and soil contamination by washing the sludge with water or weak Na_2CO_3, and to recycle the washing solution into the leaching process in step 5. This measure has not been considered in the KOBELCO process description.

5.3. General description and material flow of the nickel recovery process

KOBELCO has given a short description the nickel recovery process (June 1995). A flow chart of the process is shown i Figure 5.2, including the following steps :

1. Nickel leaching with sulphuric acid. Sulphuric acid is added to the nickel residue from step 6 in the vanadium recovery process (Figure 5.1), and then heated by injection of steam.

2. Sedimentation. Slurry from the leaching basin is thickened. The supernatant is sent to neutralization and NiS precipitation.

3. Counter current washing and thickening. The sludge from step 2 is washed and thickened in a three stage counter current decantation system (CCD-thickener). The washing solution is recycled to the leaching basin. The solid residue, containing mostly iron, is disposed.

4. Neutralization. pH is raised by adding lime ($Ca(OH)_2$).

5. Filtration. Gypsum is formed, filtered off and disposed.

6. Nickel sulphide formation and precipitation by injection of H_2S to the neutralized and and clarified $NiSO_4$ liquor.

7. Filtration. The precipitated NiS is sent to the sulphide filter for the separation of solid NiS.

8. Neutralization and discharge. The filtrate is pH-regulated with sodium hydroxide and then discharged.

Processing 25 tons ash/day will give a yield of 1,12 tons NiS/day, which means a nickel recovery rate of about 90 % from the nickel residue coming from the vanadium recovery plant (see step 6, Figure 5.1). This nickel residue also contains some vanadate, which will follow the residue from the CCD-process to disposal. Most of the nickel lost from the process will also follow the CCD-residue. In addition some nickel will follow the pore water of the residue from gypsum filtration (step 4). The nickel content in the effluent will be low due to the low solubility of the nickel sulphide

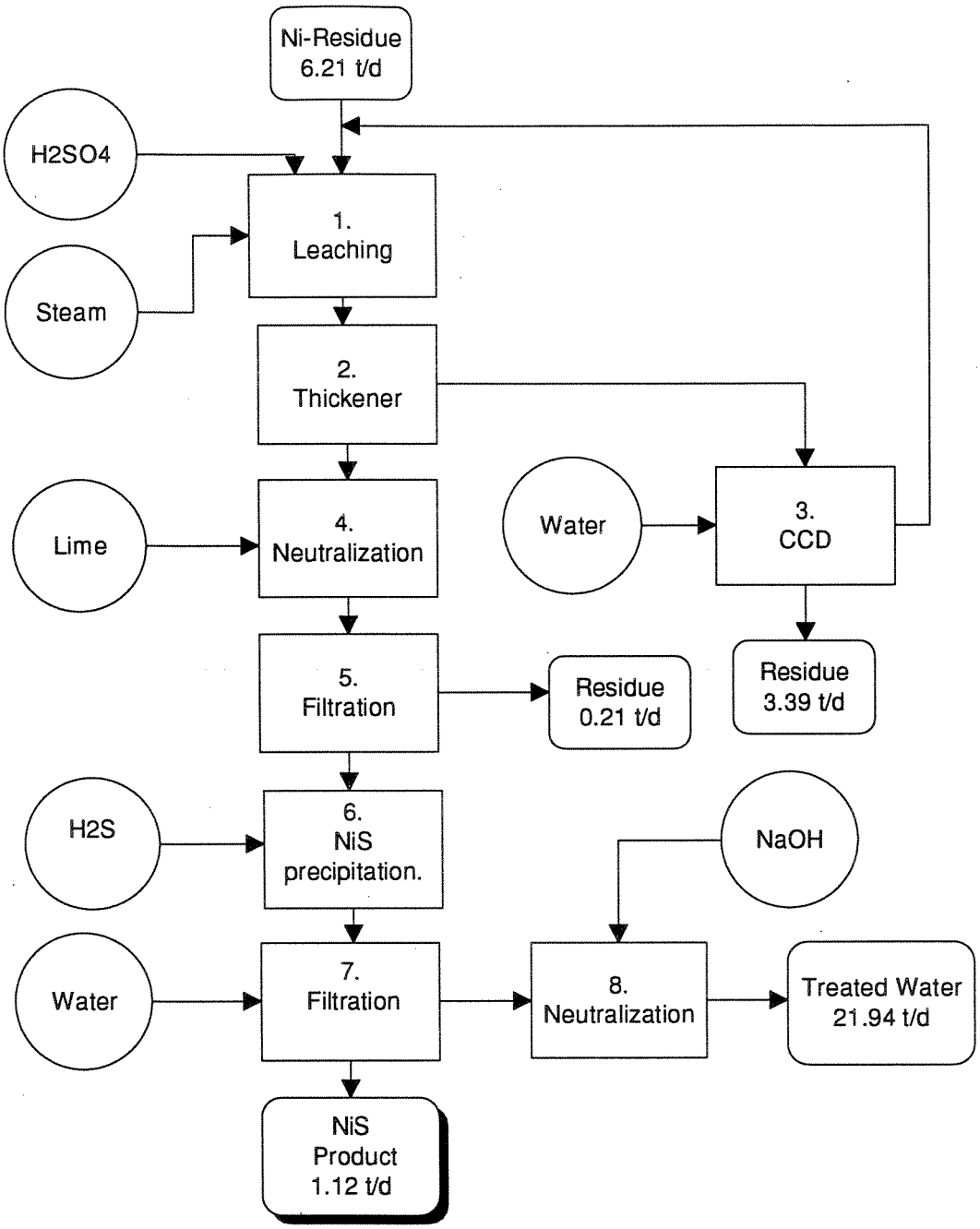


Figure 5.2. The nickel recovery process. Flow chart.

5.4. Contaminant source identification

The contaminant sources of the Vanadium and Nickel Recovery processes are presented in summary below, as far as we know them at this stage.

5.4.1. Atmospheric emissions

A short summary of the atmospheric emissions is given in Table 5.1. The issue is further discussed in chapter 6.

Table 5.1. Atmospheric emissions from the vanadium recovery plant.

Process	Dust	Ni	V	NH_3	SO_x
Melting	0,2 t/day	6 kg/day	50 kg/day		
Deammoniation				230 kg/day	
Ventilation	?	?	?	?	?

5.4.1.1. Exhaust gases from the melting process

KOBELCO has given following emission data for the melting process:

SO_x : 1500 ppm
Dust : 500 mg/Nm^3
Flow : 277200 m^3/h
Temperature : 431K (158°C)

The dust will likely contain some nickel and vanadium. KOBELCO has assumed a 98 % efficiency of the melting/leaching process. A 2% loss of vanadium and nickel represents a loss of 144 kg V/day and 17 kg Ni/day. We have no experimental data to estimate the loss to the air. As an example we suggest a loss of 50 kg V/day and 6 kg Ni/day in the subsequent evaluations.

5.4.1.2. Ammonia emissions from the deammoniation process

The NH_3 load on the scrubber is 2,3 tons/day. If we as a worst case estimate the scrubber efficiency to 99%, the loss to the atmosphere will be 230 kg NH_3/day.

5.4.1.3. Building ventilation and drying

No data are available on discharge to the atmosphere.

5.4.2. Aquatic discharges

According to KOBELCO's process description the vanadium process has two main water effluents :

- Treated water from the ion exchanger.
- Neutralised water from the deammoniation process.

The nickel recovery plant is regarded as a separate plant. As the process has not yet been decided in detail, it is not possible to provide qualified estimates for the discharges from the process.

A summary of the aquatic discharges discussed in the following chapters is presented in Table 5.2.

Table 5.2. Aquatic discharges and solid waste from the vanadium and nickel recovery plants.

Process	Nickel	Vanadium	Ammonia (as N)	Solid waste
Ion exchanger		0,3 kg/day	1,9 t/day	
Deammoniation			4 t/day	
Filtration step 8		?		?
Nickel plant	low	?		3.5 t/day

5.4.2.1. Discharge from ion exchanger

KOBELCO has given the following data for discharge from the ion exchange process :

Flow rate	: 240 m^3/day
Operation	: 300 days/year
pH in effluent	: 5,8-8,6
Suspended solids	: <200 ppm
Na_2SO_4	: 115 g/l
NaCl	: 27 g/l
NH_4Cl	: 24 g/l
V	: < 1 ppm

If released untreated this will give following loads to the recipient :

NH_4-N	: 1,9 tons N/day or 564 tons N/year
V	: < 0,3 kg V/day or < 90 kg/year. Worst case 0,3 kg /day

5.4.2.2. Discharge from deammoniation process

In the deammoniation process the liberated NH_3 is taken up in HCl in a scrubber. The neutralised ammonia (NH_4Cl) is discharged. From the vanadium content of the ash it is possible to calculate the load of NH_4Cl to the environment.

Processing 25 tons ash/day gives 7,2 tons V/day or 14 tons VO_3^-/day. This equalises 2,5 tons NH_4/day or 2 tons N/day. Thus the total load of nitrogen as NH_4 will make about 4 tons N/day or 1200 tons N/year.

5.4.2.3. Discharge from the nickel recovery plant

KOBELCO has given some data for the the composition and flow rate :

pH	: 5,8-8,6
Susp. solids	: 200 ppm
Flow rate	: approx. 22 m^3/day

The nickel content of the effluent water will be very low due to the low solubility of the nickel sulphide. The effluent may however contain some free sulphide (excess from the precipitation of NiS), and pH may have to be adjusted to ensure the area decided by law (pH 6-9)

5.4.3. Hazardous waste

The sludge from step 8 of the vanadium recovery process consists mainly of aluminium hydroxide and silica, but will also contain vanadate in the pore water. KOBELCO suggests a discharge of the filter cake to a landfill. At this stage no data are available for estimation of the loss of vanadium or amount of waste. It is possible to reduce the loss of vanadium by washing the sludge and recycle the washing solution into the leaching process in step 5 (ch. 9.1).

As a part of the emission control program we recommend a monitoring program for the water quality of the ground water and in the seep from the landfill. Evaluation of the data from this program will decide the needs for reducing the loss of vanadium.

5.4.4. Other solid wastes

In the nickel recovery process solid waste will be produced from two different process steps.

1. Residue from CCD-process with a water content of 47 %.

Component	Tons/day
H_2O	1,60
SiO_2	0,18
NiO	0,10
Fe_2O_3	0,38
$NaVO_3$	0,53
Others	0,60
Total (Wet)	3,39
Total (Dry)	1,79

2. Residue after filtration of gypsum.

Neutralization with lime will cause a generation of 0,21 tons gypsum/day as $CaSO_4 \cdot 2H_2O$ which is filtered off. The water content has not been stated. The pore water contains nickel sulphate.

The waste will have to be disposed on a landfill. A control program is recommended and described in chapter 8.

5.5. Vanadium recovery from petroleum coke (HVC-process)

During the work with this preliminary EIA, an additional process to recover vanadium from petroleum coke (HVC-process) has been discussed between KOBELCO, Lagoven and the Amuay Refinery. A brief presentation of the process and some of its environmental consequences is given in Appendix.

6. Environmental characterisation and impacts

6.1. Air Quality

6.1.1. Atmospheric emissions from the current refinery

The emission standards for SO_2 given for the Amuay Refinery, based on decree 2.225, are the following:

Maximum allowable SO_2 to the atmosphere: 75 mt/d

The SO_2 emission limit is based on a crude rate of 500 kB/d.

Maximum allowable emission concentrations from:

Furnaces/boilers	5000 mg/m^3
Coal boilers (anthracite)	2400 mg/m^3
Coal boilers (lignite)	6000 mg/m^3

The limits for emission of particulate material for power generating facilities burning solid fuel must not exceed the following levels:

Heat capacity Gcal/h MW	Emission limit kg/Gcal
Q<2.5 >2.9	2.7
Q>2.5 >2.9	3.4 x $Q_{(-.25)}$
Q>1000 1163	0.6

Emissions from the current refinery have been investigated by Diener (1994) as part of the ambient impact study for various operating scenarios. The current Refinery is assumed to operate at 450/50 kB/d of medium/heavy crude oil including the new CRAY unit. The major SO_2 sources at the Refinery today are:

Emission source	Stack height (m)	Emission rate (g/s)
Block 29, stack 1	107	960.8
Block 29, stack 2	107	960.8
DCAY F-2401	56	340.8
DCAY regenerator	61	146.0
FCAY F-2102	65	101.0
SUAY-1	46	739.8
SUAY-2	46	739.8
PSAY F-401, stack 1	59	248.2
PSAY F-401, stack 2	59	248.2
PSAY F401, stack 3	59	248.2
PVAY 5 F-451	66	226.9
CFAY, alternative 2	106	128.8
CRAY F-9101/9102	65	1.2
Total emissions		5090.5

The above emission rates are based upon R. Dieners case 2A, including a DCAY regenerator without wet gas scrubber and 90% recovery at the SUAY units 1 and 2 (Diener 1994). The total emission rate of 5090.5 g/s or 439.8 tonnes/d are at present 5 times the allowable emission rate. It is clear that several measures have to be taken to reduce these emissions.

The present ambient air pollution levels also reflect these facts, and exceedances of the ambient air quality standards can frequently be reported as presented in the present chapter.

6.1.2. Present air quality in the areas around the Amuay Refinery

6.1.2.1. Observed concentration levels

SO_2

Only a few observations of air quality in the surrounding areas of the Amuay Refinery have been made available for this study.

In a technical note dated 11 June 1990 (GER-90-183) monthly average concentrations of several air pollutants were reported from Punta Adaro and Las Piedras. SO_2 and H_2S concentrations measured from January to May 1986 are presented in Figure 6.1.

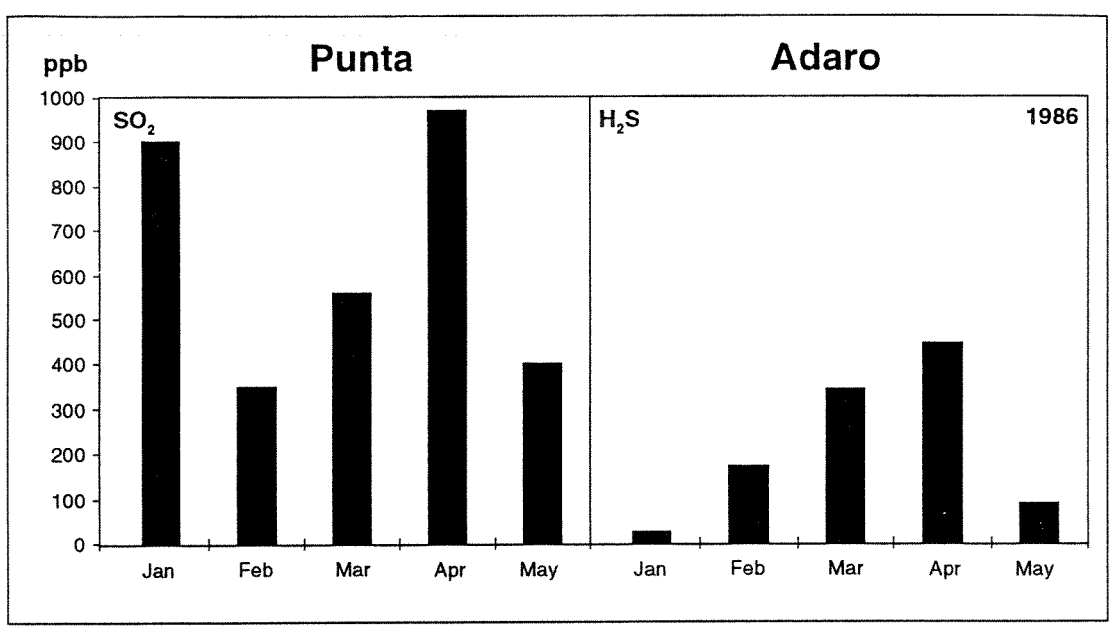


Figure 6.1. Monthly average concentrations of SO_2 and H_2S measured at Pta. Adaro in 1986.

The highest monthly average SO_2 concentration at Pta. Adaro during the first half year 1986 was 970 $\mu g/m^3$. This was five times the 5 percentile air quality standard of 200 $\mu g/m^3$. The half year average was 624 $\mu g/m^3$, which is 8 times the 50 percentile air quality standard of Venezuela. Also H_2S concentrations exceeded the air quality standards in March and April 1986.

Currently (from 20 January 1995) SO_2 is being measured continuously at Pta. Adaro. However, the range of the monitors were originally set so that peak values exceeding 0.5 ppm (1430 $\mu g/m^3$) could not

be recorded. Concentrations (integrated over less than one hour) were frequently exceeding this level during the first measuring week from 20 to 28 January 1995.

An SO_2 sampling campaign was undertaken by NILU during a site visit from 24 to 27 January 1995. A sensitive diffusion sampler for sulphur dioxide (SO_2) in ambient air has been used in several investigations to undertake a screening of the spatial time integrated concentration distribution. These samplers include an impregnated filter inside a small plastic tube. The sampler has been tested also for NO_2 and NH_3. For SO_2, the measuring ranges are approximately 0,1-80 ppb for a sampling period of one month. The equivalent range for NO_2 is 0,02-40 ppb.

At Amuay 20 samplers were located along an array about 2 to 4 km downwind from the Refinery area. A traverse of samplers were located around the monitoring station at Pta Adaro (± 2 km north-south). The results of a three day integrated concentration distribution of SO_2 is presented in Figure 6.2.

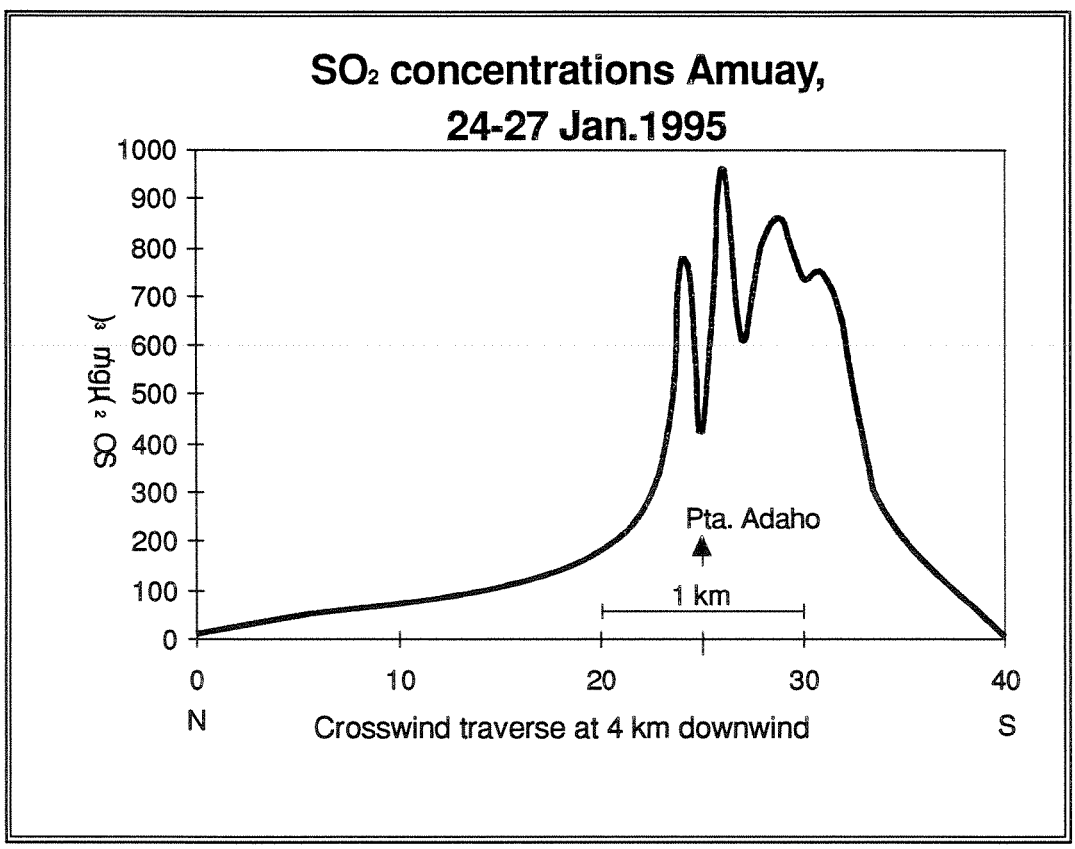


Figure 6.2. Three day average concentrations of SO_2 measured about 4 km downwind, west of the Amuay Refinery on 24 to 27 January 1995.

The highest 3-day average concentration was measured at 962 µg/m^3 100 m south of the monitoring station at Pta. Adaro. The total plume width at 4 km downwind was about 1200 m.

Total suspended particulate matter (TSP)

TSP concentrations were measured inside the Refinery close to the coke deposit in the Flexicoke area and in Las Piedras during June 1989 to January 1990. Concentrations inside the factory limits frequently exceeded the short term air quality standard of 260 µg/m^3. This value is the 0.5 percentile defined for off site air quality, not to be exceeded more than once each 5 year (MARNR decree 2.225).

It is not clear whether the measurements actually represented 24 h average concentrations, and what kind of equipment was used. This is important for considering which sizes of particles that have been collected; PM_{10} (less than 10 micrometers) or $PM_{2,5}$. Results from the measurements are shown in Figure 6.3.

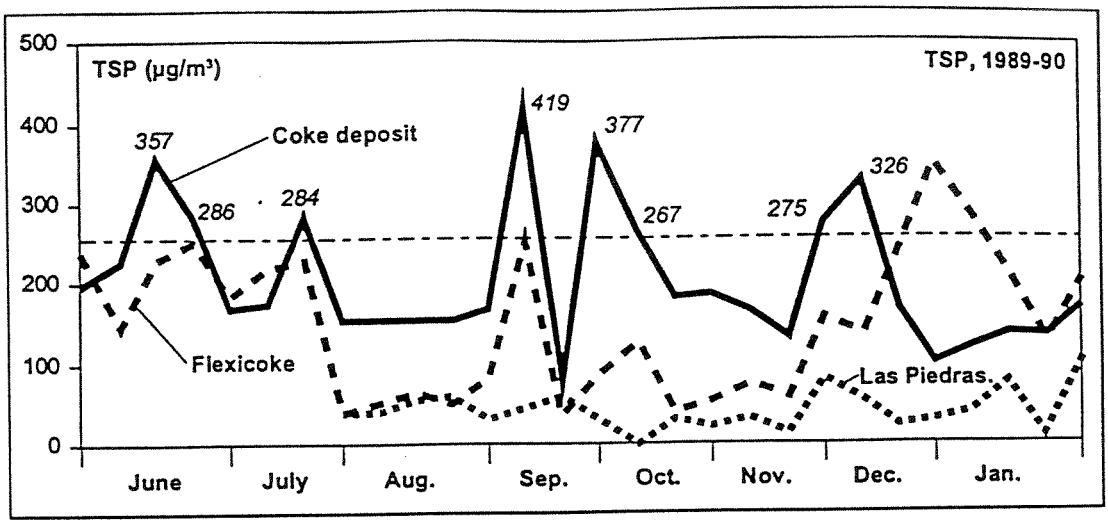


Figure 6.3. TSP concentrations µg/m^3) measured inside the Amuay Refinery area and in Las Piedras from June 1989 to January 1990.

In Las Piedras the TSP concentrations never exceeded the off site air quality standard level of 260 µg/m^3.

Other air pollutants
From the technical note (GER 90-183) no measurements of non-methane hydrocarbons (NMHC), NO_X or ozone exceeded the air quality standard values given in decree 2.225.

Concentrations of NO_2, H_2S, NMHC and ozone are presently being measured at Pta Adaro. No statistical information is, however, available. During a few days of measurements it can be seen that the levels of NO_2 are relatively low, and far below the air quality standard values of Venezuela. Also the ozone concentrations seem to be low; varying around 80 µg/m^3.

H_2S concentrations, however, were somewhat more uncertain. The highest one hour average concentrations measured during the last week of January 1995 were 250 to 270 ppb (about 380 µg/m^3). The highest concentrations were observed during night time hours.

Analyses of specific elements in the suspended dust collected on filters have not been available.

6.1.2.2. Concentration distributions from model estimates
Air pollution models linking emission rates, meteorological conditions and ground level concentrations have been established for the Amuay area (see Chapter 6.1.3.3). These type of models have also been widely used internationally to estimate the impact of existing and planned air pollution sources.

A variety of models are capable of performing such estimates:

The US EPA Industrial Source Complex (ISC) models predict concentrations of air pollutants downwind from elevated and ground level sources. ISC is routinely used in USA as part of the

permitting process both for new and modified industrial sites. The sources can be point sources (stacks) or area sources. Two versions of the ISC models have been applied; the ISCLT2 for annual average concentrations and the ISCST2 or ATDM for short term, 1 h average concentrations.

The current air quality in the area surrounding the Amuay Refinery is not in compliance with the air quality standards as given by Decree 2.225. To visualise the present air quality the results from an estimated annual average concentration distribution of SO_2 is presented in Figure 6.4.

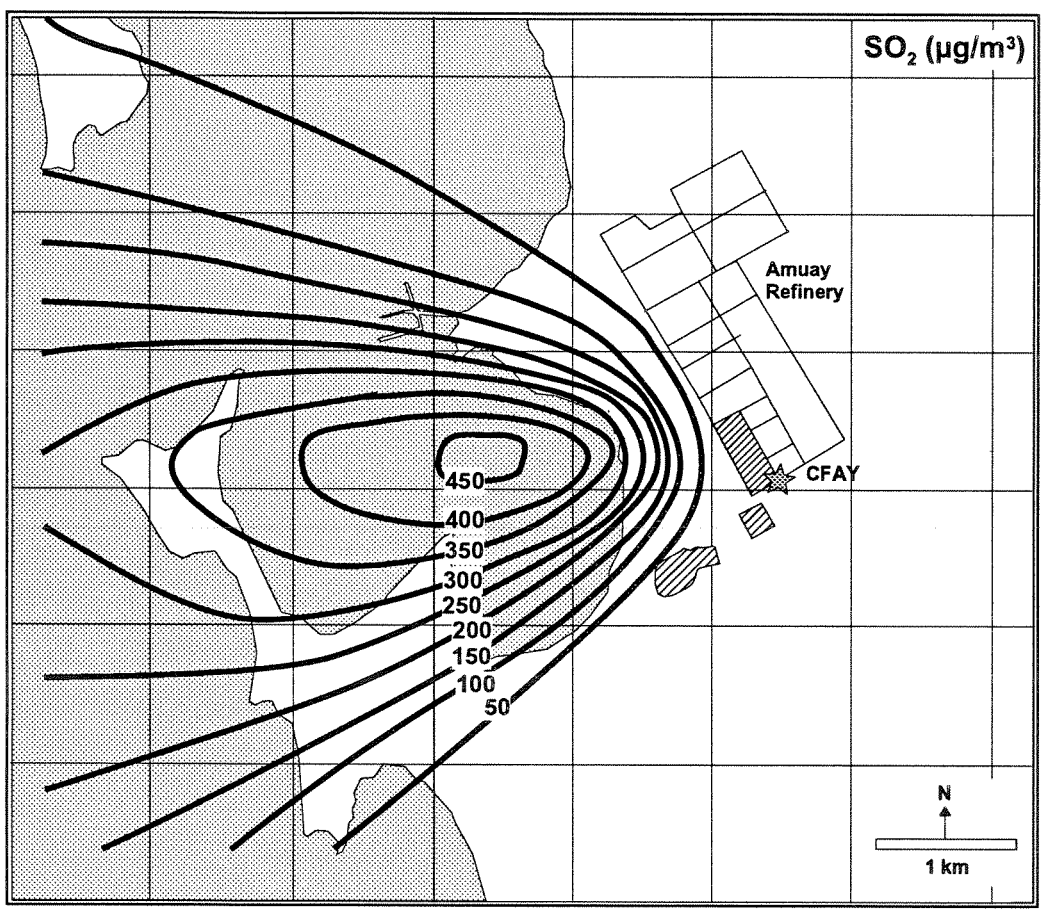


Figure 6.4. The annual average SO_2 concentration at the present Amuay Refinery (with CFAY alternative 2) estimated with the EPA ISCLT2 model.

As seen from Figure 6.4. the area of highest impact from SO_2 from the Refinery is located on the Amuay Bay. The maximum ground level concentration is found 2 km west of the Refinery area at 456 $\mu g/m^3$. Only within the first 5 km from the Refinery the air quality standard value of 80 $\mu g/m^3$ is being exceeded in an area covering about 17 km^2 . The typical annual average concentrations in the most populated areas of Las Piedras, Punto Fijo and Judibana varies from 50 to 5 $\mu g/m^3$.

The relative contribution to the annual average and to the maximum one hour average ground level concentration from individual sources is shown in Table 6.1.

The estimates of one hour average concentrations are performed for the most probable meteorological conditions; winds from east at 3-5-m/s and unstable to near neutral stability conditions.

Table 6.1. Relative contribution from selected sources at the Amuay Refinery to the maximum annual and maximum 1-h average ground level concentration of SO_2 .

Source	Annual average concentration ($\mu g/m^3$)	One hour average ($\mu g/m^3$)	Distance to maximum (m)
Whole Refinery	56	2784	
Block 29, stack1	85	350	2000-5000
DCAY-F-2401	35	300	1500-2500
SUAY-1	114	1049	1000-2000
PSAY-stack1	68	290	1500-2500
PVAY-5	20	240	1000-3000
CFAY (alt. 2)	13	132	1500-2000

The maximum concentration from the different sources does not occur at the same receptor point in the area. It is thus not possible to add the individual contributions to obtain a total impact. For this purpose a multiple source gridded model is necessary. The total impact also includes two stacks at block 29, two at DCAY, two at SUAY and three at PSAY.

As also stated by Diener (1994) the Amuay Refinery cannot be in SO_2 compliance until the overall sulphur recovery at the recovery plants has been increased to 98.5 % . SUAY-1/2 will then be the most attractive option from an environmental standpoint.

From the model estimates it can be seen that the ground level concentrations from the SUAY 1/2 alone can reach more than 2000 $\mu g/m^3$ at most. This is more than twice the State of Washington one hour limit of 1040 $\mu g/m^3$, never to be exceeded, or 5 to 8 times the World Health Organisation air quality guideline value.

6.1.3. Environment characterisation and evaluation of environmental impact

6.1.3.1. Air quality impact of the vanadium plant emissions

The future impact of atmospheric emissions from the VNRP will be compared to selected air quality standards and guide line values. As far as standards given by MARNR decree 2.225 are available, these are used.

The following criteria are referred to in the discussion:

Pollutant	Averaging time	Value ($\mu g/m^3$)	Reference
SO_2	Annual	80	MARNR Decree 2.225
SO_2	24 hour	365	MARNR Decree 2.225
SO_2	1 hour	1040	Washington state, USA
SO_2	1 hour	365	World Health Organisation
NO_2	Annual	100	MARNR Decree 2.225
TSP	Annual	75	MARNR Decree 2.225

There are very few air quality standards for vanadium available. The World Health Organisation (WHO 1988) has presented a 24 h average maximum vanadium concentration of 1 $\mu g/m^3$.

6.1.3.2. Vanadium and nickel emission data

The plant capacity is based on the combustion of 355 t/d of flexicoke in the CFAY process, producing 25 t/d of ash being the raw material for the Vanadium Recovery plant. Recovery of V and Ni are performed in two separate processes, in two different discharge effluents. The regularity of the process is estimated to 300 days per year.

We assume that the stack constructed for the CFAY project will be utilised for the combined emissions from the CFAY- and VNRP-plants. The emissions from the Vanadium plant are estimated as follows:

	CFAY	VNR plant
Stack location:	UTM coord.	x = 370415
	UTM coord.	y = 1298 070
Stack height:		106 m
Stack diameter:		5 m
Exit gas temperature (316 F):		431 K
Exit gas velocity:		3.0 m/s
Gas flow rate:	2.09×10^3 m^3/h	27720 N m^3/h
SO2 concentration in flue gas:	1200 ppm	1500 ppm
	(2203 mg/m^3)	(4290 mg/m^3)
SO2 emission rate:	128.8 g/s	33.0 g/s
TSP emission (95 % avg. removal):	12.7 g/s	2.3 g/s*
	(215 mg/Nm^3)	(500 mg/Nm^3)

* Provided 95% removal in baghouse (se ch. 7.1.1)

The SO_2 concentration at the source is close to the maximum legal limit for refinery emissions, which is 5000 mg/m^3. Assuming that the Vanadium plant will only be operated during CFAY operations, the two air flows will add and become 2.36×10^3 m^3/h, and the concentrations of SO_2 and TSP in the stack will be reduced. The total emission rate of SO_2 from the stack will be 161 g/s, the TSP emission rate 15 g/s.

If we assume that the TSP emissions contains 47 % **vanadium** the emission of vanadium from the VNRP plant will be 1.1 g/s.

6.1.3.3. Air pollution dispersion models

To estimate the future impact at ground level from planned emissions of air pollution, different type of air pollution dispersion models have been applied.

For this study two of the US EPA approved dispersion models for industrial source complexes have been established and used for the Amuay Refinery emissions. This chapter briefly describes the models.

ISC models

The US EPA Industrial Source Complex (ISC) models predict concentrations of air pollutants downwind from elevated and ground level sources. ISC is routinely used in USA as part of the permitting process both for new and modified industrial sites. The sources can be point sources (stacks) or area sources. ISC calculates concentrations at fixed receptor points defined by the user.

Two different versions of the ISC models have been used:

ATDM: A short term model for estimating 1 h average concentrations
ISCLT 2: A long term model for estimating annual average concentrations

Both models require a specification of the sources, including source location, emission rate, stack height, diameter, exit gas temperature and velocity. The user must also specify at which locations concentrations should be calculated.

The two models use different type of meteorological input.

ATDM (previously called ISCST2) needs hourly information of wind speed, wind direction, ambient temperature, mixing height and stability. Sequential data are usually taken from on site observations, which is not available at Amuay.

The ***ISCLT 2 model*** requires an annual average joint frequency distribution of wind speeds, wind directions and stability. In USA this is often referred to as the STAR-frequency distribution and has been developed for several sites where weather service climatological data are available.

A ***receptor grid*** system has been developed for the ISC models along the UTM reference system. The area covered by the models is shown in Figure 6.5.

The area covered by the model is 12 km (E-W) × 10 km (N-S) with the south-western corner at UTM (365.0, 1295.5).

The NILU model
One of several different dispersion models developed at NILU have been applied to estimate the current ambient impact of SO_2 and to estimate future impact from the Vanadium plant:

CONCX: A short term model for estimating 1 h average concentration distributions downwind from ground level, diffusive and elevated single sources. (Sivertsen 1980, Bøhler 1987)

All the NILU models have been well documented and are being used for planning purposes and for impact assessments nationally and internationally.

The CONCX model estimate concentrations during specified meteorological conditions. For CONCX several combinations of wind speeds and stability can be read into the same sequence of estimates. This makes it easy to search for the maximum ground level concentration irrespectible of meteorology.

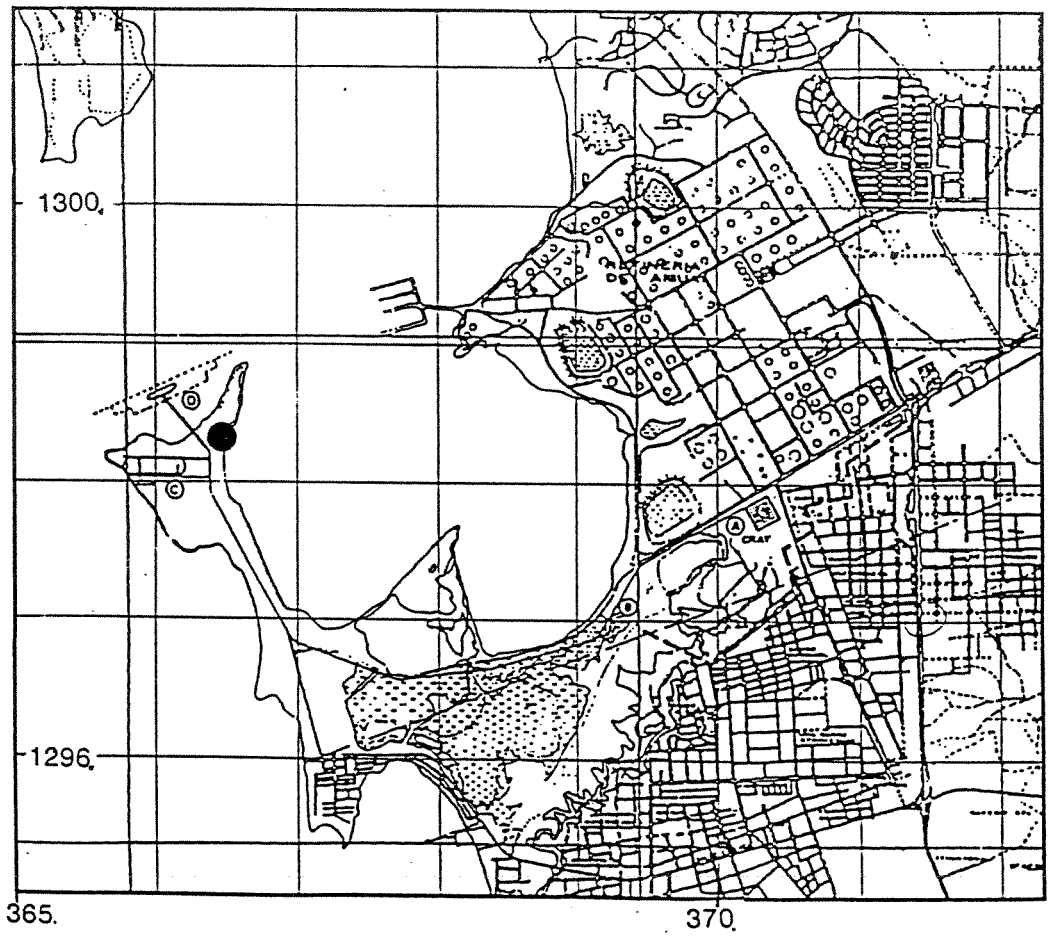


Figure 6.5. The modelling area included in the UTM reference system

6.1.3.4. Input data to models

The models need as input data some background information on;

- source characteristics and emission data,
- area characteristics (surface roughness, topography etc..)
- measurement data (measurement type, heights etc..)
- meteorological data (wind, stability, mixing height, temperatures etc..)
- dispersion coefficients (type to be used and parameters)
- dry and wet removal coefficients
- location of receptor points (distances or grid specifications)

Some of the data used in the Amuay model estimates are presented below.

Emission inventories

The emission data collected for the current refinery have been taken from the studies performed by Diener (1994). See also ch. 6.1.1.

Emission data for the Vanadium plant have been presented in ch. 6.3.2.

6.1.3.5. Future atmospheric impact

To study the future impact of atmospheric emissions from the Vanadium and Nickel Recovery Project, estimates have been performed for short term impact (1 h. average concentrations) and long term impact (annual average concentrations).

Short term impact (1 h. average concentrations)
The one hour average ground level concentrations downwind from the VNRP plant have been estimated using the models ATDM and CONCX.

The maximum ground level concentrations of SO_2 as a result of the VNRP plant is approximately 34 $\mu g/m^3$, on a distance of 1-1.5 km from the refinery (see Figure 6.6). The result is roughly the same for both type of models applied.

Compared to the air quality standard for SO_2 as given by the State of Washington USA the new VNRP plant will contribute to only 3.5 %, whereas the same emissions will contribute with less than 10 % of the World Health Organisation air quality guideline values. The emissions from the VNRP will thus not exceed the air quality standards for short term average concentrations.

Compared to the ground level concentrations resulting from the current refinery the emissions from VNRP will give ground level concentrations of SO_2 which are about 1 % of the total current emissions.

A summary of maximum one hour average ground level concentrations (1-1.5 km from the refinery) of SO_2, TSP and V_2O_5 is presented in Table 6.2.

Table 6.2. Estimated maximum 1 h average ground level concentrations as a result of the planned emissions from the VNRP.

1 hour averages	Maximum ground level concentrations ($\mu g/m^3$)		
	SO_2	TSP	V_2O_5
VNRP	33.8	2.4	1.2
CFAY + VNRP	165.8	15.4	7.4

The one hour average concentrations of SO_2 and TSP as a result of the VNRP will be well below the air quality standard values (Figure 6.6).

For vanadium we have estimated a maximum 1 h average concentration of 1.2 $\mu g/m^3$, which will result in a maximum concentration less than the WHO air quality criteria of 1 $\mu g/m^3$ (24 h average).

Based on the assumption that the VNRP will be operating together with the CFAY plant alternative 2, emission estimates for the two plants together have been performed.

Modelling results show that ground level concentrations of SO_2 and TSP resulting from both CFAY and the Vanadium plant will be below the air quality standard values both given by WHO (365 $\mu g/m^3$) and by MARNR decree 2.225 (1040 $\mu g/m^3$).

For vanadium the maximum 1 h average ground level concentration is estimated to 7.4 $\mu g/m^3$, which corresponds to a 24 h average of 3.8 $\mu g/m^3$. This is over the air quality standard values given by WHO (1987), which states that "ambient average concentrations less than 1 $\mu g/m^3$ (24 h) is not likely to have adverse health effects.

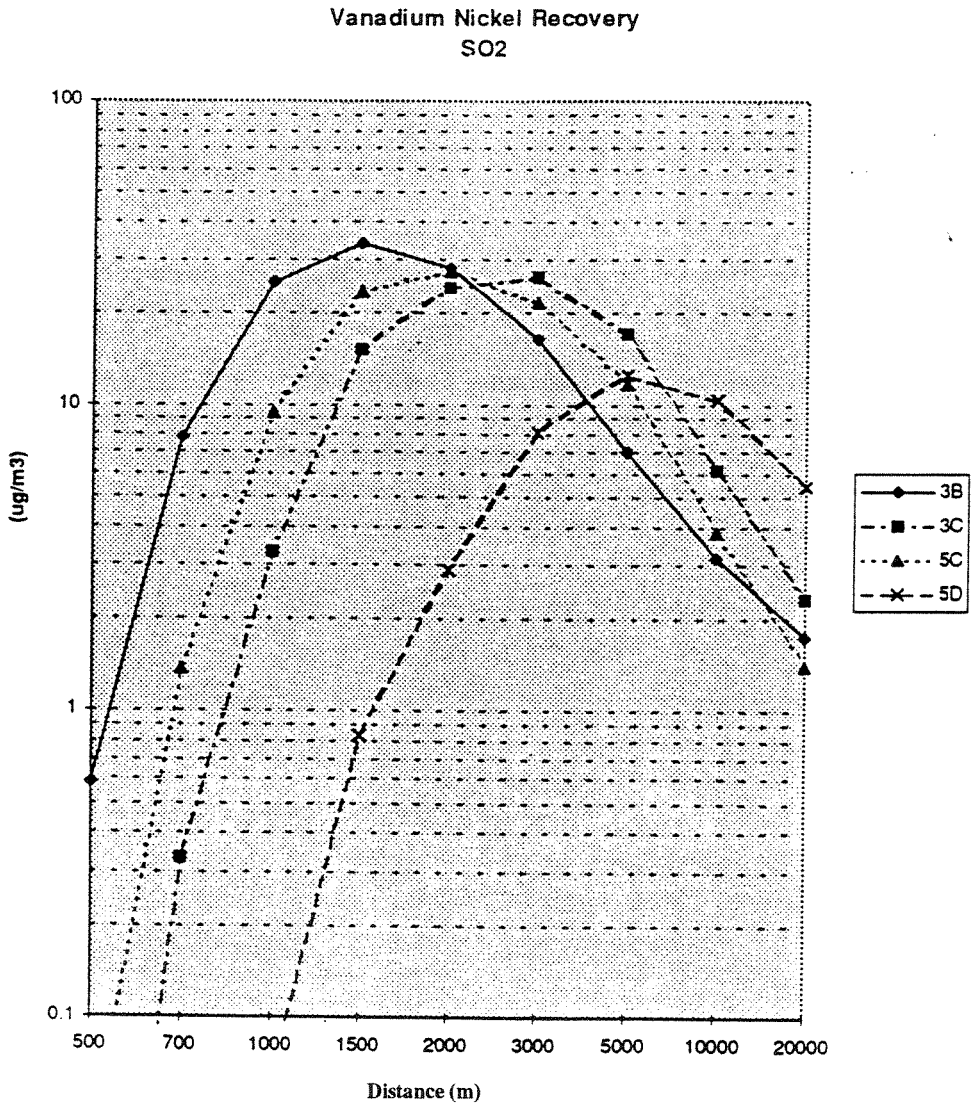


Figure 6.6. Estimated 1 h. average ground level concentrations of SO_2 resulting from emissions from the NiV plant.
3B: Light to medium wind (3 m/s) and slightly unstable atmospheric conditions.
3C: Light to medium wind (3 m/s) and unstable atmospheric conditions.
5C: Medium wind (5 m/s) and unstable atmospheric conditons.
5D: Medium wind (5 m/s) and neutral atmospheric conditions.

Annual average concentrations

The annual average concentration distribution resulting from the emissions of SO_2 from the Vanadium plant is presented in Figure 6.7.

The maximum average annual concentration of SO_2, 3.4 $\mu g/m^3$, resulting from the VNRP plant is located on the Bay of Amuay, approximately 1.8 km west of the refinery. The impact of SO_2 from the VNRP will be approximately 1 % of the impact of SO_2 from the current refinery today.

A summary of annual average maximum ground level concentrations of SO_2 and TSP are presented in Table 6.3.

Table 6.3. Estimated annual average ground level concentrations as a result of emissions from the VNRP.

Annual average	Maximum ground level concentrations ($\mu g/m^3$)		
	SO_2	TSP	V_2O_5
VNRP	3.4	0.2	0.1
CFAY + VNRP	16.6	1.5	0.7

The maximum annual average ground level concentrations of SO_2, TSP and vanadium as a result of the planned VNRP emissions are well below the air quality standard values.

For the CFAY and VNRP plants together, the maximum ground level concentrations for SO_2 and TSP are also below the air quality standard values. The vanadium concentration, however, is higher than agreeable. These levels are a result of a conservative estimate of an overall average bag house filter efficiency of 95 %. With an efficiency of 99 %, which is within the capacity guaranteed by the supplier, also the vanadium concentrations will be within safe limits.

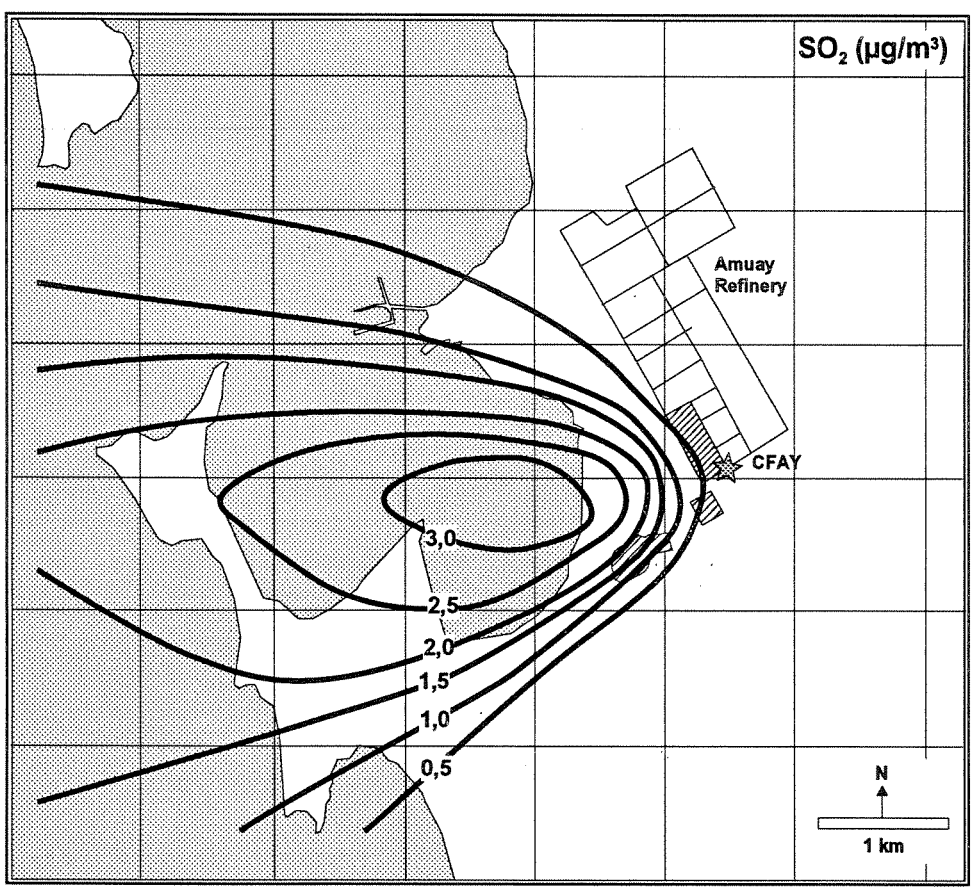


Figure 6.7. Estimated annual average ground level concentrations of SO_2 resulting from emissions from the VNRP plant.

6.2. Noise

6.2.1. Present situation

The present noise level and the estimated levels when the CFAY unit is in operation has been presented by NIVA (in prep) in connection to the CFAY EIA for 4 different locations to the south and south-west of the refinery . The final noise levels after the CFAY is in operation are presented in Table 6.4, and should be considered the environmental conditions prior to the VNRP Project. The results show that at all measuring points in Barrio La Vela the expected noise levels will exceed the official daytime norm, for one of the points with as much as 4 dBA. Also in Las Piedras slight exceedance of norm day values are expected during CFAY operation. In addition a series of night measurements in Las Piedras shows that the norm of night noise may be exceeded with as much as 11 dBA. For the sites of Al Primera, A.J. de Sucre and Zamorra the noise norms are not expected to be exceeded when the CFAY is in operation.

Table 6.4. Expected total environmental noise levels during operation of the CFAY Unit

Locations (Barrios)	**Locations/ -distance from CFAY**	**Background noise level (dBA) 1)**	**Norms 2) (dBA)**
La Vela	1/413m 2/506m 3/560m 4/745m	62.1 63.4 64.3 61.3	60 (06.30 to 21.30)
Al Primera	1/746m	61.2	60
Las Piedras	1/3518m 2/3918m 3/3838m 4 (night)/-3491m	55.2 63.0 61.1 61.1	60 50 (21.31 to 06.29)
A.J. de Sucre	1/1093m 2/1119m	58.7 58.9	60
E. Zamorra	1/1226m 2/1333m	60.9 62.5	60

1) from NIVA(in prep.) including the CFAY noise.

2) Decreto Nº 2217 "Norma sobre el control de la contaminaición generada por ruido"

6.2.2. Sources of noise

The sources of noise in connection to the VNRP will be temporary as construction noise (from vehicles, cranes and construction equipment) and permanent or intermittent as operational noise (from fans, pumps, mixers, pelletizing unit, etc.) We have not at our disposition any noise level specifications for the technical units of the Project, but for the preliminary EIA we have assumed that the same principle holds for this plant as for the CFAY plant, i.e. that no single unit shall generate above 85 dBA. In Norway this is the established working environment limit above which the use of ear protection is required. Any unit generating noise above 85 dBA should be insulated to the extent that the open air noise in the immediate vicinity of the unit is 85 dBA or less.

The localisation of the noise sources will be within the VNRP area, presumably in or close to Block 29 of the refinery.

6.2.3. Impact of the VNRP on noise

We have not at our disposition any noise level specifications for the units of the VNRP Project, but for the preliminary EIA we have assumed that the same principle holds for this plant as for the CFAY: that no single unit shall generate above 85 dBA (those above have to be sheltered). The noise modelling not only showed that the CFAY plant itself will give an insignificant contribution to the total noise level in the urban areas considered, but also that one would have to increase the number of single sources of noise emitting 85 dBA each, by a factor of more than 100, before any effects on the noise levels would be discernible. This also means that any contribution from the VNRP Plant will be insignificant.

6.3. Hydrology

6.3.1. Sites of discharge from the VNRP

The Amuay Bay is the sink for refinery cooling water and various types of process water and ballast water from the ships. Until recently the ballast water after treatment in an API separator was discharged north of the main piers, and treated process water discharged in the eastern part of the S. Bay (AWARE 1982). Now this flow goes through a brand new water treatment plant TSAY for oil residual removal before discharging into the Bay. Judibana domestic sewage also discharges into the south Bay via the Sewage Treatment Plant. The artificial lagoon receives process water via the modified API separator (Conversion Norte) for sedimentation and oil skimming before discharge to the Bay. Besides these main discharges, the Bay will receive some contaminants from the refinery through the air (fly ash, smoke stack particles), and from diffuse sources in the ground.

6.3.2. Characterisation of present environmental status of recipient waters

6.3.2.1. Surface freshwater and ground water

On basis of map and photo analysis and visits to the sites made for the CRAY EIA (Commiven 1993), it is concluded that there is no permanent surface freshwater resources (such as active rivers, creeks, and ponds) in the area of potential impact from the VNRP Project. However, occasional dry flood canals were observed that may be active during rain periods.

According to information produced by the Hydrological department of MARNR (Dirección de Hidrología y Meteorologica) there appears to be no ground water aquifers in the potential area of impact which may be influenced by effluents or leakage of contaminants from the VNRP Project or from the refinery as a whole (Commiven 1993). There are no ground water wells in use neither within the impact area nor in the surroundings.

On the other hand OHM (1993) defined two layers of aquifers (a lower below -10 m depth and an upper at -10 to +5 m depth) separated by clay seals, as a regular feature of the Amuay coastal cliffs. Under the refinery area is also found another water table above these aquifers. Geotechnical studies conducted by Lambe and Silva (1979) indicate that this perched water table did not exist prior to the development of the refinery, but has gradually increased during the lifetime of the refinery. In 1991 this water extended from about 5 to about 14 m depth beneath most of the refinery area. Under Block 29, where the CFAY and probably also the VNRP will be located, the perched water table lay at iso-bath 14 -16, or about 12-14 m below the surface. The actual source of the perched water is not known, but is believed to be within the refinery.

6.3.2.2. Amuay Bay

According to Chapter 3.2 the recipient waters for the discharge from the VNRP Plant will be the Amuay Bay, in particular the South Bay. Also the entrance to the Bay, and the coastal areas adjacent to the entrance may become affected.

The Bay is situated at the west coast of the Paraguana peninsula, just to the west of the refinery (Figure 1.1 and 6.5). The Bay is kidney-shaped, being 6.56 km wide in the NS direction and 4.18 km in the EW direction. Maximum depths, around 12 - 16 m, are found along a dredged entrance channel to the docks of the refinery. The north and south part of the Bay has in general depths less than 5 m, and the central part and the entrance has natural depths between 5 and 10 m. The opening to the Gulf between Punta Adaro and Punta del Cabo is 2,1 km wide.

The Amuay Bay water is well mixed in the vertical (little stratification). Typical temperature and salinity values are within the ranges 24-28^{o}C and 35.5-37.0 ppt respectively. The shallow South Bay has on the average 2-3^{o}C higher temperatures and 0.3-0.5 ppt higher salinity than elsewhere. The temperature difference is mainly due to the cooling water discharges which carry an overtemperature of 7-13^{o}C (NIVA 1993). Low dissolved oxygen values are reported in the area near the discharge from the Separator Lagoon. Secchi depths (measuring water transparency) is on the order of 2-2.5 m, which is little less than the average for the coastal waters (AWARE 1982). Suspended particles are in the range 1-30 mg/l in the Bay (SERVIAMBCA 1991, 1993).

Recent studies on currents in the Bay were done by Battelle (1980), AWARE (1982), ESCAM (1985), NIVA (1992, 1993). Battelle (1991) gave a review of the first three studies. Wind and the tide were the dominating forces in the model studies, which showed an anticyclonic (clockwise) gyre in the W part of the South Bay, and a clockwise gyre in the eastern part, where the main discharges are located. Direct measurements performed later by NIVA showed that the outflow of warm water from the S. Bay passes along the west shore towards Pta. Adaro, while the inflow of colder water goes along the east part of the entrance. The typical current speed at 1 m depth is 5-8 cm/s at the periphery of the gyres. The estimated mean residence time for water in the South Bay is 1.5 days.

Water exchange with the coastal region has not been studied in detail. Numerical model results (barotropic model) indicate exit flow to the north, and inflow through the southern part of the entrance between Pta. Adaro and Pta. del Cabo. Probably there is a vertical shear too, with a deep inflow that compensates for wind-driven surface outflow. One may therefore expect that there is a net outflow of contaminants suspended or dissolved in the surface layer.

The biological characterisation of the water in the Bay has been compiled in the CFAY EIA (NIVA, in prep.). The total cell densities of micro algae (the primary producers) recorded fluctuates slightly with season, and minor differences between the north Bay, the south Bay and the coast outside have been recorded. Total cell densities seem generally to be in the range 300 to 5000 cells/ml, and the number of species slightly lower than found in general for tropical regions. Total cell numbers were lower in the North than the South Bay. The difference was attributed to growth stimulation in the South Bay due to presence of low concentrations of aromatic hydrocarbons. Nitrogen is considered as the growth limiting nutrient in the coastal and Bay water. No evidence for eutrophication has been reported.

The zooplankton densities are in general rather low, and diversity and densities have been found to be clearly dependent on stochastic variations in wind velocities causing rapid shifts in the exchange of water with the coastal area (AWARE 1982). The SE part of the Bay seem to be consistently stressed with low densities of zooplankton and high dominance of a few species (AWARE 1982).

The benthic invertebrate fauna of the Bay and the coast consists mostly of nematodes, annelids, crustaceans (amphipods, isopods and crabs), bivalves, and gastropods (Bull et al. 1982, Prieto and Mendez 1990). The results showed severely stressed communities in the south-east part of the Bay with very few species present, low diversity and high dominance of nematodes and the polychaetes *Capitella capitata*, all being indicative of severe organic pollution (high organic loading and oil hydrocarbons). In the north part of the Bay the number of taxa and diversity was higher, but still clearly below the values found at the coastal bottom outside where a diverse and healthy community was recorded.

No living corals have been recorded in the Bay or at its entrance.

Along the shores of the south part of the Bay large quantities of sea lettuce (*Ulva lactuca*) were observed indicating high organic enrichment.

AWARE (1982) has listed a total of 31 species of fish from September 1981 and 23 species from February/March 1982 in the coastal and Bay area. The corresponding number of species found in the Bay itself were 28 and 17 respectively. Of bottom-dwelling fish only the gobiid *Microgobius* was taken in the south Bay. The fish investigations supports the general impression of a heavily impacted south Bay.

6.3.2.3. The coastal area

The coastal area of the Gulf of Venezuela to the west of the Amuay Bay between Punta Piedras and Punta de Amuay (Fig. 1.1) should be counted as part of the influence area from the CFAY. This part of the coastline, is running relatively straight in a SSE to NNW direction, for a distance of approximately 7 km. The depth increases gradually from the shore to about 20 m at 1000-1500 m distance outwards.

Zeiger (1964) indicated that the surface flow outside Amuay is towards north, with a deep southward return flow. Model studies of tidal currents also indicated a northward flow (Lynch et al. 1990). NIVAs measurements in 1992 (NIVA 1992) showed mainly northward flow direction 500 m offshore, but significant southward flow at times, especially near the surface. The mean of the measured current speed was 11 cm/s at 1.5 m depth and 9 cm/s at 7.5 m depth, with maxima of around 25 cm/s.

To our knowledge there is no present direct discharges from the refinery to the coastal waters. However, some of the discharges to the Bay will enter the coastal waters through the exchange between Bay water and coastal water.

At the coast chlorophyll concentrations (indicating phytoplankton biomass) as high as 5.2 mg/m^3 have been measured (AWARE 1982) which is typical for highly productive areas. Curl (1960, cited in Raymont, 1980) claimed that upwelling was mainly responsible for the high production in the Gulfs of Venezuela and Cariaco. The upwelling and hence the production is strongly seasonal with main peaks in winter/early spring and in the autumn (Sourina 1969).

In the Bay and along the coast of the peninsula the transparency is very low due to resuspended bottom particles, presence of large amount of dissolved organic matter, and blooms of phytoplankton. Also wind transported sand and silt from land makes an important contribution to the poor transparency in the sea water close to the coast. The transparency measured as the Secchi depth along the coast outside Amuay was in the range 2.4 - 4.7 m (Bull et al. 1982), which is far less than in the Caribbean Sea, and close to the shore values reported by divers are frequently less than 50 cm (USB 1992, Bakke pers. obs.).

Investigations by AWARE (1982) indicate that the nearshore zooplankton community is dominated by smaller crustaceans and by larvae during autumn and winter. Densities were in the range of 40 - 180 individuals/litre. The results indicated slightly stressed zooplankton communities. Any local seasonal

pattern in zooplankton density was neither revealed nor excluded. Very dense settlement of barnacles observed during spring (cf. below) shows that barnacle larvae must at least in winter be a very important part of the zooplankton.

Most of the sea bottom outside Amuay consist of soft sediments. The bottom material outside Amuay Bay has been characterised as well oxygenated clay and mud with some fine sand (AWARE 1982, USB 1992, NIVA observations 1992). Investigations in September 1981 and February 1982 showed that the most common group of animals were the polychaetes (bristle worms), but there was no obvious dominating species among them. In 1989 Prieto and Mendez (1990) found 32 species of sediment-living animals on the coast outside the Bay, compared to 31 in the north Bay and only 0-3 in the south Bay.

Hard bottom communities are confined to the shoreline beneath the rocky headlands, the bottom below these down to 1-2 m depth, and to stones partly buried in the sediments. Typical littoral communities like the mangrove, sea grass beds and coral reefs are to our knowledge lacking. Seasonality in animal occurrence is rather strong.

The cities of Las Piedras and Punto Fijo south of the refinery, and Amuay to the north are important fishing ports for harvesting the fish, squid and shellfish in the Gulf of Venezuela. URBANOCONSULT (1994) presents some landing statistics of fish in the region showing that sardines, guaranaro and lisa constitute about 80 % of the annual catch in the Punto Fijo - Amuay region.

AWARE (1982) found a total of 41 species of fish in catches made during the baseline investigation in 1981-82, and claim that their results supports the local fishermen's impression that the autumn fishery is the most productive.

In summary the studies show that the marine life in the south part of the Bay, and in particular the south-east Bay is severely stressed from pollution, both from organic enrichment, oil hydrocarbons and metals, and with a very poor bottom flora and fauna. The north part of the Bay and the entrance area have far healthier and more diverse communities although still showing indications of pollution stress, whereas the coastal region outside Amuay hosts a normal, healthy soft bottom community with animals living both on and in the sediment.

6.3.2.4. Present contamination status

An overview of the present contamination status of the perched and ground water resources, in the waters of the Amuay Bay and the coast outside is given below. Here we focus on liquid contaminants that are expected to be generated by the planned VNRP Plant. It is beyond the scope of this preliminary EIA to list all existing contaminant discharges to the Bay. The contaminant contribution from the VNRP is discussed in chapter 5.2.

The most recent study on contaminants in the Bay was conducted in Nov. 1991 (SERVIAMBCA 1992). They sampled for Ni, V and oil/grease in water and surface sediments respectively. Most stations were in the South Bay, with reference stations in the N. Bay, Central Bay, outside Amuay and Adaro, and N of the Paraguana Peninsula.

Their main findings are shown in Table 6.5 for the S. Bay and two reference stations. Levels both in Bay sediments and water are elevated significantly above ambient values. It may also be noted that the north Bay is less contaminated than the area outside Adaro as what regards Ni in water, and V and Ni in sediments.

SERVIAMBCA (op. cit.) also related their 1991 values of nickel, vanadium and oil/grease to previous values found in 1989-90 by Lagoven (Ni and oil/grease in water thus not covered). Their findings

showed no significant change in levels of V in water, and some higher values of V and Ni in sediments in the SE bay (near the effluent from the Laguna Artificial). Oil/grease values in the S. Bay remained high, especially near the discharges.

Table 6.5. Contaminant levels in South Bay water and sediments in 1991, according to SERVIAMBCA (1992).

PARAMETER	South Bay			N. Bay	W of Adaro
Water:	**min**	**mid**	**max**		
Ni, µg/l	0.8	2.5	7*	1.5	2.0
V, µg/l	3.6	19.2	66.5	4.5	2.8
Oil/gr. µg/l	3.4	11.5	25.9	< 10	< 10
Sediments:	**min**	**mid**	**max**		
Ni, mg/kg	16.0	250	1371	11.0	15.3
V, mg/kg	230	2615	11907	< 15	111.7
Oil/gr mg/kg	2199	83000	$3x10^3$	276	< 50

* Estacione de core sampler N^O 48, region Sur-Occidental de la Bahia.

Tissue concentrations of Ni, V and PAH have been analysed in blue crab and two species of fish from the south Bay. Only Nickel showed concentrations above the methodological detection limit. Prieto and Mendez (1987) reported tissue values of Ni in 1987 of less than 0.1 mg/kg, which may indicate an increasing trend of Ni bioaccumulation (SERVIAMBCA 1993). For Vanadium they reported values in the approximate range 0.7-1.1 mg/kg. The recent values indicate that the levels have not increased above 2 mg/kg, i.e. a smaller increase than for Ni at any rate.

Table 6.6. Measured contamination in organisms collected in the South Bay, Sept. 1993 (SERVIAMBCA 1993)

Parameter	Callinetes sapidus Cangrejo Azul		Archosargus probatocephalus Cagalona		Orthopristis ruber Coro-Coro	
	max	mean	max	mean	max	mean
Vanadium, mg/kg	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0
Nickel, mg/kg	4.6	3.3	2.7	2.5	2.7	2.5
PAH, ug/kg	< 10	< 10	< 10	< 10	< 10	< 10

6.3.2.5. Potential impact of the VNRP on the hydrological conditions

The sources of the VNRP which may have any impacts on the marine recipient are the following:

- Wet depositions from the atmospheric emissions during rainfalls
- Discharges of process water
- Drainage water from the VNRP area
- Sewage from the increase in manpower during construction and operation
- Drainage water from the deposition site for solid waste

The following compounds emitted from the VNRP to the atmosphere may be trapped in wet depositions to the Amuay Bay and coastal areas during rainfall:

SO_X
NO_X
NH_3
suspended particles
nickel
vanadium

The basis for estimating the rates of deposition, and hence the input to the Bay from this source is not existing.

The process water, drainage from VNRP area, and sanitary water from the increased manpower will all go to the new sewage treatment facility of the refinery which also serves the city of Judibana. The characteristics of these contributions to the sewage effluent (cf chapter 4) focus on nitrogen (N), vanadium (V) and nickel (Ni) and the expected concentrations at entrance to the sewage plant are compared to corresponding limits for discharge to Venezuelan marine waters in Table 6.7.

A comparison shows that the Venezuelan limits are strongly exceeded for nitrogen. As far as we know there exist no specific discharge limits for vanadium. The information about the nickel process is not sufficient to estimate the concentration in the outlet (cf chapter 5.3 and 5.4) for comparison with the discharge limit..

Table 6.7. Estimated contribution of N, V and Ni to the Amuay Bay from the VNRP.

Component	Tot. amount/day	Conc. in the outlet	Venezuelan limits
Process water	262 000 l	-	-
Nitrogen	3900 kg	16 200 mg N / l	10 mg N / l
Vanadium	0,3 kg	1.25 mg / l	?
Nickel	?	?	2,0 mg Ni / l

Information is not available to discern the fractions in dissolved or particulate form. One must expect that most of nitrogen (as ammonium ions) is in solution and hence will pass through the sewage treatment plant without significant loss. The nickel and vanadium residues are mostly particulate, and although the size distribution of the particles is not known, one must expect that some of this material is retained in the settling pond of the sewage treatment plant, and that only the smaller particles will be discharged to the Bay.

With the shallow depth and the mean residence time of 1.5 days for the water in the south Bay (cf chapter 6.3.2.2) there is a possibility that some of these particles may sink to the bottom in the Bay. The sediments of the Bay consist of sandy clay and silt, indicating deposition conditions. On the other hand since the particles are small, they are also most likely to be kept in suspension in the Bay water and be transported to the coast. As long as the particle retention efficiency of the treatment plant is not known, one can neither estimate how much of the nickel and vanadium from the VNRP which will pass on to the Bay, nor how much of this material which will be retained in the Bay sediments.

As a worst case scenario one may postulate that all the particulate material from the sewage and process waters passes the treatment plant and settles in the Bay. The process water from the VNRP contains less than 200 mg/l of particulate matter (cf. chapter 5.4.2), and it is reasonable to expect from other studies that the sewage contains about the same. The process water volume is 262 m^3/day, and sewage 1425 m^3/day (approximately 9500 persons each using 150 l/day), giving a total water flux of app. $1{,}7 \times 10^6$ l/day, containing 340 kg/day of particulate matter and 300 g/day of vanadium. The vanadium concentration of the settling particulate matter to the Bay will on this basis be 880 mg/kg at the most. Compared with the corresponding concentrations in the bottom sediments of the South Bay (cf. table 6.5) it appears that these concentrations are within the range of concentrations already found in the sediments.

This implies that even a heavy sedimentation of contaminated particles from the effluent should not cause any significant changes in the contamination status of the bottom of the south Bay with regard to vanadium. An efficient particle retention in the sewage treatment plant will greatly improve this situation, and therefore comply with the main objective for the future: a gradual clean up of the Bay.

There may also be a contribution of vanadium to water from step 6 (Filtration to nickel cake) and step 8 (Filtration of sludge to deposit) cf. chapter 5. Based on a 90 % recovery of the vanadium from the ash there will be a total waste production of 700 kg V/day. Most of this is linked to the solid waste. There is not enough information to estimate how much of this will enter the Bay through leaching and runoff, but this input can be minimised through appropriate waste handling and storage (ch. 6.4.3.2.).

The nutrient addition to the Bay from the VNRP represents 16.2 g nitrogen / l in the outlet. This is an extremely high value, over 1600 times higher than the Venezuelan limit. Options to reduce effluent nitrogen are discussed in ch. 7.

6.4. Ground and soil areas

6.4.1. General characterisation

Two main types of landscapes have been identified within the study area, characterised by erosion and accumulation respectively.

The erosion areas are characterised by landscapes formed on sedimentary rocks (clay and limestone) from the late Tertiary, and with a very low inclination (1-2 %). The erosion areas can be divided into 3 sectors:

a: The erosion plains. These have inclination of 1-5 % and are reasonably stable geologically. They may be further divided into a lowland area close to the shore with elevation of about 4-10m above sea level, and higher plains behind the regressive edges (see below) with elevation of more than 20 m.

b: The regressive edges. These are very conspicuous along the NE shore of the Bay. They represent a constant edge destruction of the higher erosion plains. This area is very instable and has strong restrictions on urban use, due to the highly sensitive geology.

c: The rocky shore headlands. These are found scattered along most of the west coast of the peninsula. In these sectors one may observe large movements of material of various types and phases of wave erosion. The landscape is very instable, which prevents utilisation of the ground for permanent activities.

Accumulation areas are very scarce, primarily since the semiarid climate does not allow formation of any extensive depositional areas on land. The dynamics of the coastal water allow smaller depositional areas to form in certain areas along the shores, accumulating clay, sand, limestone, and organic matter.

The assumed location for the establishment of the VNRP installation, Block 29, lies within the refinery production area at about 28 m above sea level. The area must be considered to belong to the higher erosion plains, although the geomorphology of the refinery area in general has been severely changed by construction activities over the last 40-50 years.

A stratigraphic profile of the Amuay geology, as compiled by Dr T.W. Lambe (OHM 1993), shows that the Amuay cliff consists of a 2-5 meter cap of caliche (calcite cemented sand stone) overlying a silty sand which varies in width and depth throughout the refinery. A very plastic brown fat clay underlies the silty sand. This fat clay layer acts as an aquitard separating an upper perched water zone from the underlying upper aquifer. The soil below the brown clay is referred to as a silty clay and contains the upper aquifer. The upper aquifer is hydraulically connected to the Bay of Amuay. The silty clay is underlain by a layer of grey fat clay which separates the upper and lower aquifers. Below the grey fat clay there are alternate layers of silty clay and sand containing the lower aquifer.

The area of industrial usage within the zone of impact is primarily represented by the refinery installations which occupies about 693 ha. The development of the refinery since the late forties has seriously changed the gross geomorphology of this area although the main features such as the upper plain and slanted hillside towards the Bay is still recognised. The construction of the road and conveyor line to Pta Adaro in connection to the CRAY project has to some extent, but not extensively, modified the landscape along the southern shore of the Bay. Also the old residential area of the refinery south of Adaro, demolished long time ago, modified the hillside along the coast somewhat. The concrete remnants of the houses are still a conspicuous feature of this area. Recently intensive deposition of soil material between the saline pond and the flexicoke storage site of Yankee Stadium to the south of the Bay has covered up the original soil surface. In this connection the old local cemetery situated in this area has been moved to a new site at Los Taques.

6.4.2. Contamination levels in soils

Information on the present soil contamination status of the impact area is limited to analyses performed by OHM (1993) in and around Yankee Stadium, and assumptions of general hydrocarbon contamination of the ground containing the perched water table (Geotecnica de Venezuela, 1993).

The soil and ground water well analyses performed by OHM (1993) show that soils in one location south east of the storage site are contaminated with hydrocarbons and metals, in particular copper, mercury, and vanadium. However, soil samples taken close to the dumpsite towards west and north-east were not. Furthermore, there were no indications that the coke from within the Yankee Stadium had contaminated the underlying soils. We have no other information on the contamination levels in the soils in and around the refinery area. It is, however, likely that contaminants from the runoff water from the flexicoke storage facility accumulate in the soils of the lowlands close to the Bay to the west of the facility. Possibly these contaminants will also sooner or later enter the Bay.

6.4.3. Impact of the VNRP on geomorphology and soil contamination

6.4.3.1. Impact on geomorphology

During construction of the VNRP excavation and levelling work is expected to be confined to Block 29, and will therefore not have any impact on the surrounding geology or geomorphology. During operation a storage site for the solid wastes (cf chapter 5.4) will have to be selected. We have received no

information as to the proposed handling of this waste, except that it will have to be stored in the refinery area. The storage arrangements should be planned so that the visible appearance of the stored material is minimised. One alternative that might be considered is to use the material as part of the capping for the closure of the present flexicoke storage facility at Yankee Stadium. This would however demand for a gradual capping procedure, which may conflict with the aim of rapid solution to the present flexicoke flash problem.

6.4.3.2. Impact on soil contamination

There are three potential sources of soil contamination from the VNRP. One is the risk of spill of ash, chemicals, and the different intermediate products during the process. There are however no information available about the security procedures for the different stages of the process.

The other two potential sources of soil contamination are wet depositions from the air emissions and drainage water from the potential storage site for solid waste from the neutralisation step of the nickel recovery plant and the aluminium sulphate precipitation step of the vanadium recovery plant.

We will advice that the deposition site is constructed to avoid mobilisation of these metal residues (watertight membrane bottom, capping, drainage water pipeline system etc.). If not, it is assumed that metal contaminated pore water will be leaking from the waste material to the ground beneath and further on to the Bay. The basis for estimating the magnitude of such mobilisation is, however, not present.

7. Recommendation for preventing and mitigating actions

7.1. Proposal of actions to prevent or minimise environmental impacts

7.1.1. Cleaning systems for gas emissions

The emission figures presented in ch. 6.1.3.2 assume no gas cleaning, except for the combination with the CFAY baghouse cleaning to benefit dust reduction.

The emission concentrations of SO_2 coming from the melting process (stage 3, Figure 5.1) has been estimated to 4290 mg/m^3, which is close to the limit (5000 mg/m^3) given in decree 2.225 for furnaces and boilers. If treated in the CFAY baghouse and released from the CFAY stack, SO_2 from VNRP will be diluted to approximately 2600 mg/m^3, which will be the concentration of the mixture of CFAY and VNRP flue gas.

The SO_2 emission rate from VNRP is estimated to 33.0 g/s, which is 0.65% of the current refinery emission rate, and 3.8 % of the allowable limit defined in decree 2.225 for a crude rate of 500 kB/d.

If connected to CFAY Alternative 1, which include flue gas cleaning and desulfurization in sea water scrubber, the SO_2 reduction will be 97%, which means a stack emission rate of approximately 1 g/s.

Compared to the total Refinery SO_2 emission, the VNRP contribution is considered negligible. However, to reach the allowable limit of 75 t SO_2 /d to the atmosphere, the introduction of scrubber treatment for SO_2 absorption for new projects will represent a starting point.

7.1.2. Cleaning and recycling of waste water

The effluent flow rate from the vanadium recovery will be 240 m^3/day or 167 l/min, carrying 3.9 t NH_4-N/day (1.9 t from ion exchanger and 2 t from NH_3 scrubber) or 2.700 g NH_4-N/min. The concentration will be 16.2 g N/l.

The legal concentration limit for total nitrogen discharge is 10 mg/l, which means that the effluent water will have to go through an extensive treatment.

A brand new process water treatment plant (TRAY) was put into operation in April/may 1995, for the cleaning of the fresh water effluents coming from the sulphur stripping (SWAY 3/4; 2750 l/min) and from other refinery processes (2800-3200 l/min) (Hernan Trujillo pers. comm.). The effluent treatment includes 5 steps:

1. Desulfurication step. Cooling by heat exchanger from 110°C to ambient temperature and thereafter desulfurication (only SWAY effluent, 2750 l/min).
2. Oil recovery step. Separation and recovery of oil (general process effluent only, 2750 l/min).
3. Flotation step. Mixing of both streams. Coagulation by adding sulphuric acid, sodium hydroxide (pH-adjustment) and coagulant. Flocculation by adding polymer. Flotation for oil recovery (combined streams, 5550-5950 l/min).
4. Decantation step followed by dehydration of sludge.
5. Treated water discharge via Artificial Lagoon to Amuay Bay.

The plant has been designed for a hydraulic capacity of 6000 l/min and a nitrogen content of up to 160 mg/l in incoming water, which means a treatment capacity of 960 g N/min. The N content in treated water for discharge to the Bay shall not exceed 10 mg/l, which is the legal maximum limit.

From the estimates presented above, it seems obvious that the TRAY effluent treatment plant will have the hydraulic capacity, but not the treatment capacity to take care of the effluent water from the VNRP-plant to bring the N-content under the legal limit of 10 mg N/l to the recipient.

A high degree of recycling of ammonium chloride from the ion exchange process and from the ammonium scrubber will be necessary to reduce the amount of nitrogen in the effluent water to 10-20% before introduction to the TRAY plant. Technically, recovery of ammonia and recycling of most of the ammonium chloride used in the process, is possible. However no such techniques are presented in KOBELCO's process description.

Sour water stripping may be an alternative to reduce the NH_3-N to 10%. Surplus NH_3 goes to flare for release to the atmosphere as NO_x. This solution will have to be considered in association with the total NO_x emission from the Refinery, compared to the legal limits.

There are 4 existing sour water strippers in operation at the Refinery today. It is uncertain whether one or more of these have vacant capacity to take care of NH_3 from the VNRP project.

pH adjustment of the waste water may be necessary to ensure an effluent pH within the legal scale (pH 6-9).

The vanadium discharge is estimated to 0.3 kg/day as a worst case, and will mainly be connected to particulate matter. This will lead to an increase in the vanadium content in the dehydrated sludge, which means that the sludge should be handled as hazardous waste.

It will, however, be possible to recover a considerable amount of vanadium by washing the sludge from step 8 (Figure 5.1) with water or weak Na_2CO_3, and thereafter recycle the washing solution into the leaching process in step 5. This will reduce the vanadium loss, and thus also the vanadium concentration in the effluent water and in the filter cake, which has to be disposed to a landfill.

The effluent flow rate from the nickel recovery will be 22 m^3/day carrying 200 ppm of suspended solids. Some excess sulphide may follow the effluent after the precipitation of NiS. Therefore pH adjustment of the effluent water may become necessary to obtain the legal pH (pH 6-9). The nickel content of the effluent has not been stated by KOBELCO, but will probably be neglible due to the low solubility of NiS.

7.1.3. Solid waste handling and treatment

At this stage we have no information about the amount of sludge coming out of step 8 in the vanadium recovery process. The filter cake will consist mostly of aluminium hydroxide and silica, and the pore water will contain unknown amounts of vanadium. As mentioned above the vanadate concentration can be reduced by washing and recycling.

KOBELCO assumes that the filter cake should be disposed to a landfill. The landfill will have to satisfy the design and construction standards given in provisions from the Venezuelan government 23. April 1992, Article 26 and 28-29, including multiple barriers against water/soil escape.

According to KOBELCO the nickel recovery process will generate approximately 3.6 t/d of solid waste when using lime for the recovery. This relatively inert waste material may be utilised as landfill cover, for instance as a top layer over the disposed filter cake from the vanadium recovery (above).

The residue from the CCD-process (Step 3, Figure 5.2) will contain vanadium (as vanadic acid), representing a loss of 0,53 t/d of Na VO_3, which means 0.22 t V/d. A washing procedure (CCD-process) of the nickel residue (from the vanadium recovery process) prior to the nickel leaching is recommended to improve the vanadium recovery.

7.2. Justification, location, efficiency and costs of actions and equipment.

The proposal given above for gas cleaning includes only equipment already planned for the CFAY process, which means no extra costs for the VNRP project.

The recommended water cleaning actions include recycling/recovery, sour water stripping, and cleaning in the already existing TRAY water treatment plant. The need for sour water stripping capacity depends on the amounts of ammonium chloride that one is able to recycle in the vanadium recovery process. If there is available capacity to combine the sour water stripping of the VNRP effluent with existing streams, this will represent an economical saving. If not, a new sour water stripper may have to be constructed for this process. As the recycling capacity is uncertain, it is not possible to estimate the watercleaning costs at the present.

According to the information received from the refinery, no location has yet been pointed out for the disposal of solid waste from the VNRP project. As the amounts and content of hazardous material included in the solid waste is still uncertain, it is not possible for the moment to estimate the costs of the mitigating actions of the landfill.

7.3. Conclusions related to environment

From an environmental point of view, the most critical part of the VNRP is the high N-content of the effluent water. Water treatment to obtain an acceptable (legal) N- concentration (<10 mg/l) will make the project environmentally acceptable. Gas cleaning including particle removal (CFAY baghouse) and SO_2 reduction (sea water scrubber) is also strongly recommended.

8. Evaluation of major risks and proposal of guidelines for surveillance and control

8.1. Vanadium. Health and environmental risks

8.1.1. Environmental levels and exposures

In remote areas like the South Pole, the concentrations of vanadium in air ranges from 0.001 to 0.002 ng/m^3. Natural sources of airborne vanadium are marine aerosols and continental dust, and the levels in ocean air in the middle latitudes are about two orders of magnitude higher than the South Pole values.

Vanadium concentrations in the air of remote rural areas are less than 1 ng/m^3. Other rural areas show concentrations in excess of 50 ng/m^3, generally reflecting the local burning of fuel oil with high vanadium content. Typical concentrations in urban air may range from below 1 ng/m^3 to over 300 ng/m^3, with annual averages for large cities of about 20-100 ng/m^3.

Vanadium concentrations in air in the vicinity of metallurgical industries are often about 1 µg/m^3. In production of vanadium metal or compounds, concentrations may reach a few mg/m^3. In boiler-cleaning operations, dust concentrations are frequently around 50-100 mg/m^3, and concentrations as high as 500 mg/m^3 have been reported. The vanadium content of the dust is about 5-17% as vanadium pentoxide and 3-10% as lower vanadium oxides. The need for personal protection devices in such operations is obvious.

Drinking water supplies without excessive vanadium pollution contain from less than 1 µg/l to occasional maximum concentrations of 15-30 µg/l. A typical range is 1-30 µg/l, with an average of about 5 µg/l.

Food is considered as the main source of vanadium intake for the general population, with concentrations in the range of 0.1-10 µg/kg wet weight, and typical concentrations of about 1 µg/kg. Estimates of daily intake suggest a range of 10-70 µg with the majority of estimates below 30 µg (WHO 1988).

From the large amounts of dissolved vanadium having been carried out into the oceans throughout all geological periods, vanadium levels in sea-water of about 60 mg/litre might be expected. In fact, levels do not exceed 0.003 mg/l, indicating that vanadium is continuously removed from sea-water.

It has been concluded that vanadium content in sea-water is not dependent on solubility, and that natural reagents remove vanadium from the water. There are two possible pathways, namely sorbtion and biochemical processes. The bulk of vanadium reaching sea-water is precipitated from the water by ferric hydroxides and organic matter. Reaching the seabed it becomes bound to silts.

Biochemical reactions play an important role in the extraction of vanadium from sea-water and conversion into a sediment. This is confirmed by the link of between the concentrations of vanadium and organic substances in sedimentary rocks and silt.

8.1.2. Evaluation of health risks of vanadium

Exposed workers may suffer from irritation of the eyes and the respiratory tract. There is a dose-response relationship between the concentration of vanadium in air and its irritant effect. With short-

term inhalation exposure to vanadium pentoxide at a concentration of about 0.1 mg/m^3, irritation is manifested as coughing with increased production of mucus. Continuos exposure to even lower levels (0.01-0.04 mg/m^3) may cause some irritation, but does not impair lung function.

A reversible decrease in forced vital capacity (FVC) has been reported with exposure to a dust containing 15% vanadium at a level of about 0.5 mg/m^3. Higher exposure levels of 5-150 mg/m^3 cause atrophic rhinitis and bronchitis with a risk of bronchospastic effects. Eczematous dermatitis may occur with low-level exposure to vanadium pentoxide (6.5 µg/m^3).

Non-specific effects, such as headache, nausea, weakness, ringing in the ears, and palpitation, have been reported in exposed workers. These effects have not been related to any specific level, but, on such occasions, it has been taken as an indication of the need of personal protection in work tasks, associated with the risk of heavy exposure to dusts containing vanadium.

Available data do not imply any risk of carcenogenic effects, however the data cannot be considered conclusive. Available data suggest that vanadium may be embryotoxic and gonadotoxic (WHO 1988).

In terms of occupational exposure, the most important vanadium compounds are vanadium pentoxide, vanadium trioxide, ferrovanadium, vanadium carbide and vanadium salts, such as sodium and ammonium vanadate. The oxides and salts are commonly used in industry in powder form, giving rise to the possibility of dust and aerosol formation, when the substances are crushed or ground. Many metallurgical processes involve the production of vapour containing vanadium pentoxide, which condenses to form respirable aerosols. Boiler-cleaning operations generate dusts containing the pentoxide and trioxide compounds. Combustion of residual fuels with a high vanadium content is likely to produce aerosols of the pentoxide as well as oxide complexes of vanadium with other metals.

Breaking, loading and unloading, crushing and grinding, and magnetic separation of vanadium slag causes thick dust formation, with concentrations ranging from 30 to 120 mg/m^3. The slag contains 1-129 g vanadium pentoxide/kg. A diameter of less than 2 µm was recorded for 70-72% of the particles, 86-96% had a diameter of less than 5 µm. When the slag is roasted, free vanadium pentoxide discharged into the vicinity of furnaces ranged from 0.04 to 1.56 mg/m^3 (WHO 1988).

The smelting and granulation of technical vanadium pentoxide are accompanied by the formation of an aerosol which escapes when the product is poured for granulation. During the loading of smelting furnaces, concentrations of vanadium pentoxide ranged from 0.15 to 0.80 mg/m^3. During the smelting and granulation, concentrations ranged from 0.7 to 11.7 mg/m^3. In other parts of the work-place, concentrations may range from 0.03 to 0.2 mg/m^3.

During the drying, sieving and calcination of ammonium vanadate and during crushing, unloading and packaging of pure vanadium pentoxide, dusts are formed. When vanadium pentoxide is sieved after calcination, the concentration in air may range from 2.2 to 26 mg/m^3. In plants with less mechanisation, incomplete sealing of equipment, and inefficient local exhaust ventilation, concentrations of dust during these operations ranged from 4.9 to 48.9 mg/m^3 (WHO 1988).

High-volume sampling and atomic absorption analysis have been used to measure vanadium pentoxide concentrations in the air at several places in a vanadium refinery. The highest concentrations (>1mg/m^3) were detected in samples collected during the removal of the vanadium pentoxide flakes. High-volume samples from other locations as well as low-volume samples obtained over 6.5-h work shifts showed lower concentrations (0.002-0.735 mg/m^3; WHO 1988).

Significant occupational exposure to vanadium-containing dust occurs during the cleaning of boilers. Most of these operations are carried out by hand, and the dust in the air inside the boilers may range

from 20 to 400 mg/m^3, the most common range being 50-100 mg/m^3, with the dust containing 5-17% vanadium pentoxide and from 3 to 10% of the lower vanadium oxides.

8.1.3. Effects on organisms

Live marine plats and animals play an important role in the biological migration of vanadium. Ascidians and holothurians are noteworthy vanadium accumulators. Some marine algae are also capable of accumulating vanadium. When they die, these organisms promote accumulation of vanadium in the silt.

Thus, vanadium dissolved in sea-water is continuously removed either by sorbtion or biological processes. In the first case, the main precipitant is hydrated ferric trioxide, in the second, vanadium is accumulated by marine animals, plankton, and, less commonly, algal and plant organic material.

Trace quanities (1-10 µg/l) of vanadium stimulated the growth of some algae, including *Scenedesmus* or *Chlorella*. Toxicity studies on phytoplankton, mainly using pentavalent vanadium, have revealed differences in susceptibility between various species. A concentration of 0.02 mg/l, as ammonium vanadate, interfered with the cell division of the freshwater algae *Chlorella pyrenoidosa*, whereas 0.25 mg/l was lethal. The 15-day LC_{50} for an estuarine and salt-water green algae (*Dunaliella marina*) was given as 0.5 mg/l of sodium metavanadate, and that of a salt-water pennote diatom (*Asterionella japonica*) as 2 mg/l (WHO 1988).

Some marine invertebrates, such as the tunicates, accumulate vanadium to levels that may be 10^{-5} to 10^{-6} times the sea-water concentrations. Vanadium levels in such species may exceed 3000 mg/kg dry weight. It has been stated that uptake of vanadium in the mussel *Mytils edulis* from food (plankton) was of the same magnitude as that from water. It appears that benthic aquatic organisms tolerate higher concentrations of vanadium than fish.

Available studies on vanadium toxicity on fish have been performed on fresh-water species only. Hardness is considered an important factor influencing the toxicity, and the LC_{50} values are higher in hard water (WHO 1988).

8.2. Monitoring program

The operation of the VNRP calls for a program for monitoring of emissions. The program should be in accordance with requirements given by M.A.R.N.R. (Decrees No. 2,224 and 2,225, April 1992, about control of aquatic and air emissions), and co-ordinated with the on-going and future monitoring of total refinery emissions.

Monitoring strategies should be in compliance with latest international standards and recommendations on methods, where continuos developments are taking place (Mukund et al. 1995, Intergovernmental Task Force 1992).

The objectives of a continuous environmental monitoring programme will be:

- Identify the highest impacted areas from a given source or source area,
- or to identify the relative impact of different sources or source categories,
- observe trends and development in time,
- evaluate impact in urban or populated areas,
- evaluate compliance with environmental quality standards,

- provide a data base for evaluating effects of all kind,
- develop and verify environmental quality models,
- evaluate the impact of reduction strategies,
- monitor general background concentration levels.

The selection of sampling sites and the number of sites depend on the characteristics of the sources, and types of emissions. This chapter gives some general recommendations and strategies for the eventual future environmental monitoring program related to VNRP. Implementation and conduction of the program requires production of a detailed manual, including time schedule, sampling parameters and stations, analysis procedures etc.

8.2.1. Surveillance and control of air emissions from VNRP

8.2.1.1. Air quality monitoring programme

If utilising the CFAY gas cleaning facilities and stack, as recommended in ch. 7.1 above, the air monitoring programs of the two projects will have to be combined. A permanent monitoring programme at two or three selected sites, may be designed based upon the wind frequency- and population distributions. SO_2 should be measured continuously at all sites. NO_2 and ozone at one site downwind. PM_{10} and $PM_{2.5}$ should be sampled at least once a week for gravimetric analyses and analyses of nickel and vanadium.

The location of the sampling stations must be selected to assure that the data collected are representative and meet the objectives of the measurements. Each station must be located so that it is not imposed by nearby buildings, topography or other physical constraints. The measurements must not be strongly influenced by local sources and activities.

The selection of monitoring sites requires considerations about sources, transport and dispersion conditions. Before the final selection of monitoring locations, simple dispersion model estimates should be undertaken. Estimates of expected maximum impact areas can be derived from simple models or be taken from diagrams established for this purpose.

Sampling time and frequencies should be decided based upon

- source characteristics; continuous, intermittent, point/area/line-source,
- pollutants to be considered, reactivity and deposition,
- expected pollution levels and potential effects,
- averaging times specified in air quality guidelines.

In general the data must contain enough information to establish the necessary averages relevant for considering environmental exposure, impacts and effects.

Three types of monitoring stations should be selected for future air quality impact assessment:

1. Heavily polluted area, representative for the expected maximum impact.
2. Expected impact populated area, considering all source categories (industry/ energy/traffic).
3. Low impacted populated area or reference station/ background regional pollution.

The location of the automatic sampling station at Pta. Adaro will meet most objectives and is representative for monitoring site type 1 for heavily polluted area. Data should be stored in the database as hourly values, and frequency distributions, maximum values and average values for various averaging times (corresponding to air quality guidelines) should be established. Air quality data should

also be compared and correlated with meteorological data collected from the meteorological tower at the monitoring station.

To get a more complete picture of the general air quality in the Amuay area (Las Piedras -Punto Fijo - Judibana) simpler monitoring stations could be located in Punto Fijo and Judibana. Meteorological data could be taken from Pta. Adaro, which is representative for the larger area. Continuous records of SO_2 and daily samples of PM_{10} (Hivol), NO_2 and VOC should be collected.

8.2.1.2. Fugitive dust surveillance and sampling

The fugitive dust emissions from CFAY, VNRP and Yankee stadium and the impact of these emissions can and should be studied in more details. A combination of simple two filter samplers downwind at different distances from the storage area may be used for sampling. Wind speed and other meteorological variables should be monitored to enable the establishment of quantitative relationship between emissions, fluxes, concentrations, deposition of dust and toxic elements. In this way it would also be possible to establish an improved model for estimating future impacts from the storage area.

Together with one or two fixed particle sampling sites located at different distances downwind it will be possible to design an experiment which would answer the problems linked to the resuspension of dust from the storage area.

8.2.2. Surveillance and control of water discharges

The main objective of the monitoring is to assess the amounts of pollution that discharge into the Amuay Bay from VNRP. An initial control and monitoring program lasting 1 year should be followed by an evaluation on the demand for permanent monitoring.

8.2.2.1. Effluent monitoring

Effluent water should be specifically monitored during the first year of operation, to assess both the exact discharge rate and the main contaminants, which are expected to be TSP, Ni, V, N and non-volatile hydrocarbons.

Separate monitoring systems for the quality of effluent water from both the vanadium- and nickel recovery plants should be established. If utilising the TRAY water treatment plant, the samples should be collected upstream of the treatment plant, and at the outlet to the Bay. The parameter list for analysis should minimum include TSP, particle size distribution, N, Ni, V and total organic/inorganic carbon.

Sampling should be part of the permanent monitoring on the refinery, after evaluation of the 1st year results.

8.2.2.2. Ambient water quality monitoring

If treated as recommended in ch. 7.2 above, the VNRP effluent water discharges will add only a few percent at most to the existing contaminant fluxes. The refinery already has a program for monitoring the water quality of the Bay. This program should continue, with enhanced monitoring of TSP, nitrogen, vanadium, nickel and pH in the S. Bay.

The program should be combined with the establishment of a PC-based numerical model of circulation and water quality within the Bay and exchange with the coastal waters. This model should be implemented in the total environmental monitoring and control program of the refinery.

The exchange of water and contaminants between Amuay Bay and the adjacent coastal water in the Gulf of Venezuela should be assessed by continuous current measurements in the entrance. This may be done with bottom mounted doppler current profilers which measure currents acoustically at several depths without disturbing the ship traffic.

M.A.R.N.R. recently initiated an investigation on the impact of industrial waste on marine waters in eastern regions of Venezuela, and several negative impacts were identified (Roberts et al. 1994). A similar approach should be taken also for the effluents from the larger discharges on the west coast of the Paraguana Peninsula.

8.2.2.3. Monitoring of marine sediments and bottom communities

Marine communities may be subject to accumulation of toxic substances in the sediments. As outlined in chapter 2 the contamination status of the south Bay is severe, and the community of sediment living organisms is very poor. Although it is the intention of Lagoven to improve the conditions in the Bay by reducing the input of contaminants not only from the VNRP effluents, but also from other sources, one must expect that the recovery time will be very slow due to the large stock of contaminants in the sediments. It may be necessary to perform some remedial actions in the Bay itself to improve the situation (e.g. dredging, capping), but any decisions should be made on a thorough assessment of the extent of the contamination. Hence, we propose that the monitoring programme in the Bay is adjusted to include core samples to deeper layers of the sediments to assess the depth of contamination. Cores should be taken in e.g. two transects across the Bay from the refinery shore, one from the new cooling water discharge and towards Pta Adaro, and the other from the TSAY effluent and beyond the Bay entrance including at least 2 reference stations on the coast. The core samples should be sectioned to as deep as possible and each section analysed separately for the contaminants in question, metals (primarily Ni and V), oil hydrocarbons, and PAH. Some samples should also be analysed for chlorinated hydrocarbons (PCB) which may be formed as a result of the chlorination process. The results of the analyses should be used to assess how much of the contaminants are stored in the sediments in the Bay, to what depth, and if the contamination increases towards the sediment surface (indication of an active source) or decreases (indicative of older deposits). Further monitoring should be performed every second or third year to assess any changes in the conditions.

As long as the sediment contamination remains stable at the present conditions, no improvement in the bottom fauna can be expected. It is therefore not recommended that any extensive monitoring of the bottom communities is done until the chemical monitoring of waters and sediments shows any improvement in the situation.

8.2.2.4. Surveillance of fish contamination

Only a few investigations on fish contamination has been conducted in the area, including Amuay Bay (SERVIAMBCA 1993a). The parameters included Ni, V and PAH. Compared to previous studies, tissue concentrations of especially Ni had increased, to values around 2.5-2.7 mg/kg (ref. para. 2.7.3.2). These values correspond to about 5-10 times expected background levels in coastal areas (Knutzen and Skei, 1990), and do not by themselves represent any danger for fish consumption (there are in general no international or other satisfactory food quality limits for nickel in fish). However, due to the signal of bioaccumulation of nickel in fish from the Bay and considering the importance of local fisheries and the public interest, monitoring of contamination levels particularly in commercially important species of fish should become part of the regular monitoring of the refinery, possibly in co-operation with the Pta. Cardon refinery for the coastal monitoring. Since we do not anticipate any contamination in the coastal fish stocks, the purpose would primarily be to produce evidence of this to the market. The parameter list should include Ni, V, and the lipophilic PAHs and PCBs.

8.2.3. Surveillance and control of noise

According to chapter 6.2 it is not expected that the VNRP will produce any significant noise addition during operation. The total noise level of the refinery operations even before the VNRP eventually comes in operation, is expected to exceed the Venezuelan noise norms in some areas. It is therefore recommended that the noise measurements performed prior to the VNRP establishment are repeated

once after the VNRP is in operation, to verify the theoretical assessments made for the CRAY, CFAY and VNRP noise emissions.

8.2.4. Surveillance and control of solid waste

Solid waste from the VNRP process, including dust (fly-ash) collected by the CFAY baghouse filters, damaged or used filters and other ash-contaminated material, should be treated as hazardous waste due to its high contents of Ni and V and its fugitive characteristics. The light, fine particulate ash will easily be mobilised by wind, if exposed. Particular precautions to avoid atmospheric and human exposure must be taken.

The deposit of sludge from the vanadium recovery process will have to satisfy the design and construction conditions given by M.A.R.N.R. The deposit should be equipped with wells for ground water quality monitoring of, at least, pH, Ni and V. A monitoring program should be developed during the first year of operation.

8.3. Program for information of the environmental status

Environmental monitoring and mitigating actions related to the VNRP construction and operation phases should be properly announced within the refinery. Surrounding communities should be held informed about the developments through newspapers and other media. The benefits from constructing the VNRP should be emphasised.

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Appendix

Vanadium recovery from petrolium coke (HVC-process)

A1. Vanadium recovery from petroleum coke (HVC-process)

A.1.1. Process description

Two flowchart presented by KOBELCO are shown in Figures A1 and A2. Vanadium is extracted from petroleum coke as vanadate under alkaline conditions. After washing of the residue, the combined filtrates containing vanadate (VO_3^-) runs into the ash recovery process at step 7. The residue containing mostly carbon will probably have to be disposed to landfill or burned in the CFAY furnaces.

In step 1 (Figure A2) petroleum coke is dispersed in water. After addition of sodium carbonate and heating the vanadate is extracted under addition of H_2O_2 as an oxidant. Unsoluble matter is filtered off and washed with water. After a new filtration step the filtrate containing recovered vanadate from the pore water is mixed with the first extract. The combined extracts runs into the vanadium recovery process in the step after filtration of the nickel residue (Figure A1).

The HVC process has no effluents. The carbon rich residue can be disposed on landfill or burned in the CFAY plant.

KOBELCO has given following material balances for the HVC process :

		Coke	Leaching	Washing	Comb. filtrate	Residue
V_2O_5	tons/d	1,73	1,33	0,28	1,61	0,12
SiO_2	tons/d	0,06				0,06
NiO	tons/d	0,04				0,04
Fe_2O_3	tons/d	0,02				0,02
SO_3	tons/d	0,82				0,82
Carbon	tons/d	10,92				10,92
Total	tons/d	13,59	1,33	0,28	1,61	11,98

Total water demand for the HVC process: 24,85 m^3/d. The vanadium yield of the process is 93,1 %.

A.1.2. Consequences for the boiler ash extraction process

We suppose that no changes are made in this process concerning material flow or water demand (240 m^3/d). If introducing the filtrate from the HVC process into the V_2O_5 process, the water load on the ion exchanger will be increased with about 10 % to 265 m^3/d. Consequently the discharge of ammonia from the ion exchanger will increase to 2,1 tons NH_4/day or 620 tons /year.

The HVC process will increase the production of V_2O_5 with 12,5 % (from 12,8 tons V_2O_5/day to 14,4 tons/day). The released ammonia from the deammoniation process will increase from 2,5 tons NH_4/day to 2,9 tons NH_4/day. The total discharge of NH_4 including the effluent from the ion exchanger will be 5,0 tons NH_4/day or 3,9 tons N/day.

The emissions to the air from the scrubber will increase from 230 kg NH_3/day to 260 kg NH_3/day. If burning the released ammonia from the deammoniation process in stead of trapping in hydrochloric acid, an amount of 2,7 tons NH_3/day will generate 4,8 tons NO_2.

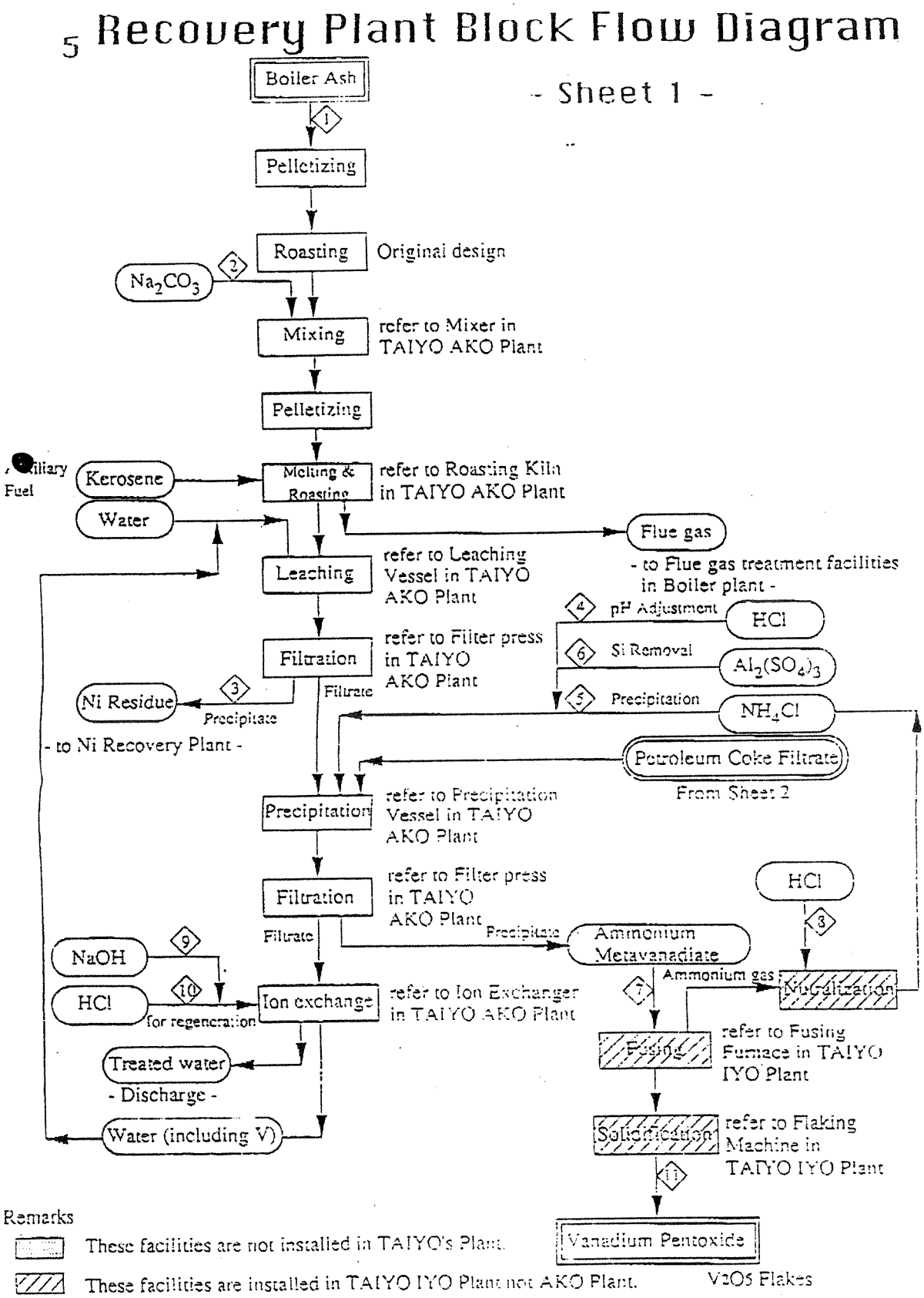

Figure A1 (See text)

Recovery Plant Block Flow Diagram

- Sheet 2 -

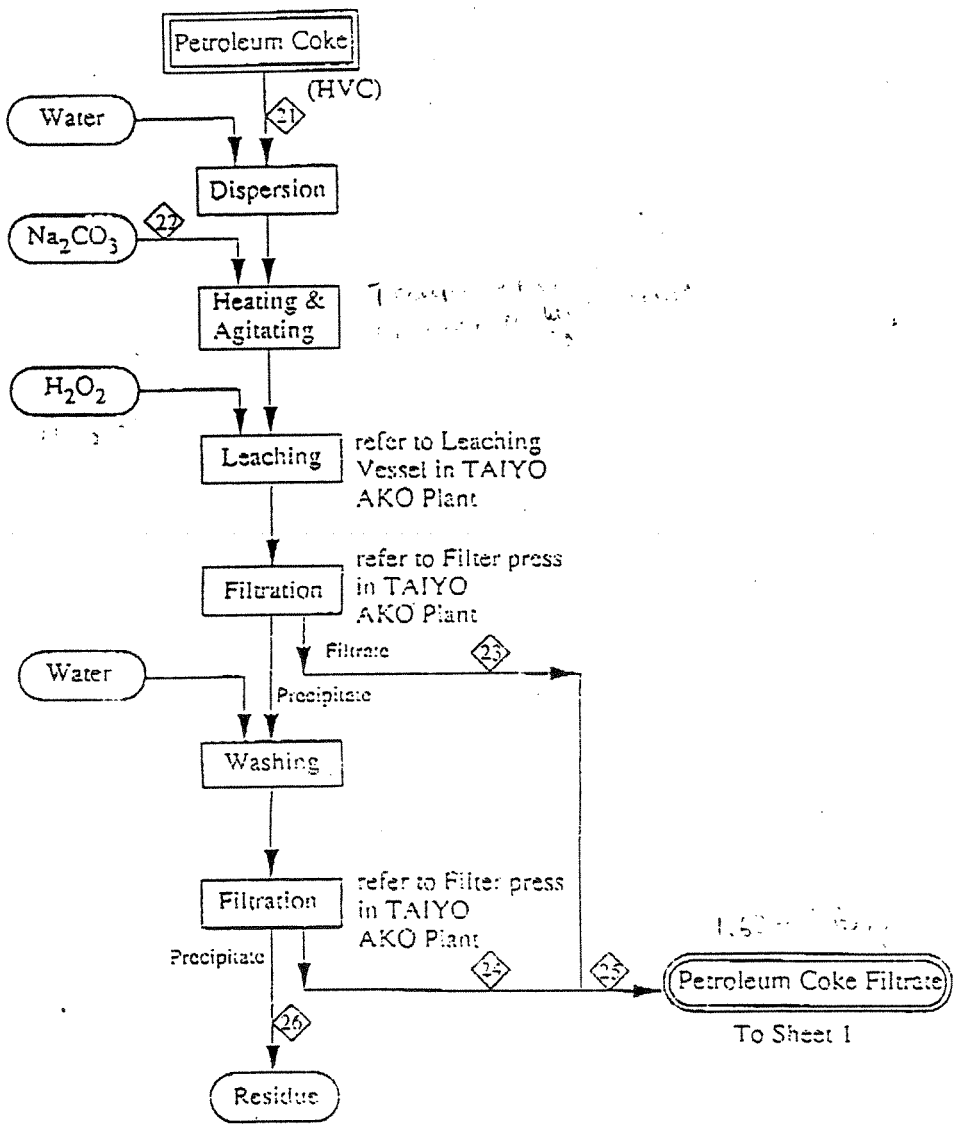

Figure A2 (See text)

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