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TECHNICAL ASSISTANCE FOR THE PETROCHEMICAL INDUSTRY IN ALGERIA WITH A VIEW TO IMPROVEMENT OF ITS PERFORMANCE AND EXPANSION OF ITS PRODUCTION

SI/ALG/87/803

ALGERIA

Technical report: Mercury cell restoration compared with replacement by membrane cells*

Prepared for the Government of Algeria
by the United Nations Industrial Development Organization,
acting as executing agency for the United Nations Development Programme

Based on the work done by A. J. Walkley, expert on salt electrolysis

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EXPLANATORY NOTES

Exchange Rate	$1.00 = 4.85 Dinars.
MEICIP	Ministre de l'Energie et des Industries. Chimiques et Petrochimiques, Algeria
ENIP	Enterprise Nationale de la Petrochimie, Algeria.
TEC	Toyo Engineering Corporation, Japan.
VCM	Vinyl chloride monomer.
PVC	Polyvinylchloride.
PTFE	Polytetrafluorethylene e.g. Teflon.
KA	Kiloamperes.
KWh	Kilowatt - hours.
Kg/cm^2	Kilogrammes force per square centimetre.
ppm	parts per million (10^6) by weight.
ppb	parts per billion (10^9) by weight.

ABSTRACT

Modernisation of Salt Electrolysis Plant (existing mercury based)

SI/ALG/87/803

The mission visited the Complex de Matieres Plastiques of ENIP at Skikda, Algeria from 6 January to 29 January, 1988 to study the mercury cell salt electrolysis plant there and to consider improvements including the possible replacement of the mercury by membrane cells.

The plant is described and its problems are discussed section by section.

The proposal by ENIP to replace the mercury cells by membrane cells is examined and compared with restoring them to their design condition. On the basis of an approximate cost comparison, it is concluded that there is no economic justification for installing membrane cells, but it is recommended that this should be checked by more detailed studies. The environmental problems associated with mercury cells can be overcome as judged by all technical standards, but it is not known whether these are acceptable to the public generally. The case for membrane cells will rest largely on this issue.

Some general characteristics of membrane cells and their merits are discussed and it is concluded that, so far, an insufficient number of membrane cell suppliers have been considered to make a proper selection of the best technology, if it should be decided to install them. It is recommended that more be consulted.

The mercury losses of the plant are analysed and recommendations are made to reduce them.

The disposal of mercury contaminated waste solids is considered and it is suggested that these be dumped into a monitored land-fill site as practised in the U.K. and elsewhere.

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INTRODUCTION

The salt electrolysis unit of the Complex de Matieres Plastiques of the Enterprise Nationale de la Petrochimie (ENIP) at Skikda was designed during 1972-76, constructed and finally commissioned in 1979. It uses the mercury cell process for the manufacture of chlorine and caustic soda.

The design period coincided with the development of widespread concern over the environmental effects of mercury and the design was modified to include provision for mercury conservation. The design finally approved and implemented was excellent in this respect.

However, operation of the plant since 1979 has been poor, never attaining more than 25% of design capacity and also exhibiting large losses of mercury to the environment.

Following discussions between the Ministre de l'Energie et des Industries Chimiques et Petrochimiques (MEICIP), the Enterprise Nationale de la Petrochimie (ENIP) and representatives of UNIDO and UNDP during 1986 and 1987, a decision was taken to send a UNIDO expert on a mission of one month to Skikda to assist the staff of ENIP to diagnose the problems of the plant, to make recommendations for improvement and, in particular to consider whether to convert the plant to operate with membrane instead of mercury cells.

On arrival at Skikda on 6 Jan 1988, the mission was told that the management of ENIP had already decided to convert the plant to the membrane cell process.

The mission, therefore, adjusted the emphasis of its activity to examine the existing plant in general to determine the actions necessary to restore it to an acceptable state and to confirm whether the decision to convert to membrane cells could be supported.

The mission then went on to consider the methods which should be used for disposing of the existing accumulation of mercury contaminated sludge and mercury contaminated rubble and scrap metal which would be produced during the conversion of the cells.

Finally the mission assisted ENIP officials in consideration of the conversion to membrane cells and in the selection of the membrane cells to be installed.

RECOMMENDATIONS

Mercury cell restoration

It is recommended that the capital cost of restoring the mercury cells to their design condition should be established in detail.

TEC should be asked to prepare a quotation for supplying the necessary components and supervising their installation.

The work should include the replacement of all base-plates and end-boxes and replacement or relining of side-channels. Ancilliary equipment such as mercury pumps, flowmeters and pipework should also be checked.

Action ENIP
UNIDO

Contractors for membrane cells

Additional membrane cell contractors should be included in the consideration of the membrane cells. It is recommended that ICI Chemicals and Polymers and Uhde GmbH should be asked to make proposals.

Action ENIP
UNIDO

Comparative costs of alternatives

Detailed and accurate operating costs should be prepared for the mercury cell restoration case and the membrane cell conversion case, so that these may be combined with the appropriate capital costs and a firm well-founded choice be made.

Action ENIP
UNIDO

Plant improvements

The studies for the redesign of the salt handling and resaturation should continue as and when the quality of the salt supplied is clarified. Brine mist filters should be installed and serious consideration be given to replacing the Nash chlorine compressor by a radial turbo-compressor system.

Action ENIP

Chlorine liquefaction

This plant should be recommissioned and as soon as practicable and a hazard analysis be arranged for the storage of liguid chlorine.

Action ENIP

Salt industry

Whatever other actions are taken to improve the salt electrolysis plant, the poor quality of salt available is a great handicap. Representation should be made to MEICIP to review the salt industry to develop a grade of industrial salt comparable to that available for salt electrolysis plants elsewhere.

Action ENIP
UNIDO

Recommendations made irrespective of cell room modifications

The following measures should be implemented without delay as they are desirable whatever the future cell room configuration may be.

Waste disposal

A widespread search should be made for a suitable land-fill site which can be used for the establishment of a monitored tip. Collaboration with the mercury mine at Azzaba is suggested. Information about waste disposal practice in Europe should be sought from the Bureau International Technique du Chlore, Brussels. (Reference 1)

Action ENIP

Replacement programme for rubber-lined items

This should be developed and initiated as soon as possible as component failures may increase to unacceptable levels by the end of 1990, the earliest date for membrane cell conversion.

Satisfactory alternatives to the neoprene cell covers are known, such as PTFE- faced neoprene. These should be installed to stop chlorine leaks.

Action ENIP

Mercury conservation

Measures to improve mercury cleanliness and recovery should be developed together with an accounting system by a special team responsible for this. Weighing of mercury in the cells to establish the loss per cell-day could await the outcome of the restoration-conversion study, because it will involve capital expenditure which would be wasted in the event of the plant being converted to membrane cells.

Mercury hygiene procedures should be instituted in line with internation standards.

Mercury-rich sludges from caustic filtration and hydrogen chilling should be treated to recover mercury directly only the settled aqueous effluent be sent to the waste water treatment section.

Hypochlorite treatment of the brine purification sludge should be restarted.

Action ENIP

I DESCRIPTION OF THE CHLORINE PLANT

A Salt handling and Resaturation section

Salt is brought to the site from Biskra by rail and off-loaded into an uncovered storage area. Near Biskra both salt made by natural evaporation from brine from a salt lake (chott) at Megheir and crushed crude rock salt or refined salt in available at Aourir. From the stockpile salt is conveyed vertically in a bucket conveyor to the top of two elevated resaturators where the salt is dissolved in brine depleted in strength by its passage through the electrolysis cells. The brine thus restored but containing impurities from the salt is passed to the brine purification section.

B Brine purification section

A small side stream is treated with calcium chloride to precipitate calcium sulphate. After allowing the calcium sulphate to settle, this stream is re-united with the main stream from which calcium carbonate and magnesium hydroxide are precipitated by adding sodium carbonate solution and caustic soda respectively, together with a flocculating agent. The suspension is passed to a thickener, the clarified overflow of which is filtered in sand filters, acidified and fed to the electrolysis cells.

The underflow sludge, after being combined with the settled calcium sulphate sludge and other mercury contaminated sludges, is dewatered on belt filters.

Provision is made for the dewatered sludge to be repulped with dilute hypochlorite liquor for the extraction of mercury before a final second dewatering. At present, however, this process is not used, but a small amount of sodium sulphide is added to the sludge to fix the mercury as the very insoluble mercuric sulphide before it is disposed of to waste.

C Cell room

The cell room contains 18 $30m^2$ Mitsui Toatsu mercury cells operating at 210 KA maximum, producing 110t/day chlorine, 125t/day caustic soda and 3.1t/day hydrogen.

Purified brine is electrolysed between coated titanium anodes at which chlorine is discharged and a cathode comprising mercury flowing down a slightly inclined steel base plate. Sodium deposited in the mercury as an amalgam is reacted with water in a separate vessel and the mercury is recirculated to the electrolysis cell.

The depleted brine leaving the cells is dechlorinated by vacuum, followed by air blowing and by treatment with sodium thiosulphate before being returned to the brine resaturation section.

D Chlorine handling section

The hot chlorine gas from the cells is cooled in two stages with cooling water and chilled water, passed through a blower into three sulphuric acid drying towers in series.

The dried gas is compressed in a Nash liquid ring compressor to $2.2Kg/cm^2$, sealed with sulphuric acid before passing to the liquefaction section.

E Chlorine liquefaction section

The chlorine gas is condensed to liquid by a refrigeration system, which also provides chilled water for use in other parts of the plant. The liquid chlorine can be stored in eight 200t chlorine spheres designed for operation at $8Kg/cm^2$ pressure, protected by a common bund. Liquid chlorine can be vapourised from this system for transmission to the vinyl chloride monomer plant (VCM).

The residual gases from the chlorine liquefiers, small amounts from vessel venting and gas from the brine dechlorination system is absorbed in caustic soda to make sodium hypochlorite.

F Caustic soda filtration

The caustic soda liquor as produced at the cells contains graphite particles and finely divided semi-colloidal mercury in suspension. These are removed in a candle filter pre-coated with activated charcoal reducing the mercury content of the caustic soda to less than 0.5 ppm. Periodically the precoat becomes fully charged and is removed by backwashing the filter, being replaced by a new precoat. The discharged precoat material is combined with the waste water before the alum clarification stage of the waste water treatment.

G Hydrogen treatment section

Hydrogen leaves the electrolysis cells fully saturated with mercury vapour. The gas is cooled with process cooling water in indirect contact coolers at the individual cells, the condensed mercury returning to the cells, but the combined hydrogen gas stream from all the cells is then chilled in a direct contact scrubber to circa 15°C, before compression for combination with the fuel gas system. The condensate accumulating in the scrubber passes to the waste water mercury recovery system.

H Waste water treatment section

Water affluents from the areas of the site in which mercury is present, namely the cell room, brine resaturation, brine purification, brine dechlorination, caustic soda filtration and hydrogen cooling and compression, are collected separately from water draining from other areas of the site and are conducted to the waste water treatment section. These effluents comprise floor washings, spillages, rain water, etc.

Here it is first made mildly alkaline (if necessary), alum is added and the flocculated sediment is settled in a thickener.

The overflow from the thickener is passed successively through two anionic exchange resin columns for mercury removal followed by a chlelating resin mercury removal column before being discharged to the sewer containing circa 20 ppb mercury.

The anionic exchange resin can be regenerated with ammonia. Mercury is recovered from the regenerating fluid by distilling off the ammonia, separating the precipitated mercury ammonia complex by centrifuge and recovering the metallic mercury from this by distillation in a small retort. The chelating resin cannot be regenerated.

The underflow from the thickener is combined with the sludge from the brine purification thickener before this is dewatered.

I Anhydrous caustic soda section

70% caustic soda liquor produced at the cell is evaporated to 100% in an evaporator using molten salt as heating medium. The anhydrous caustic soda is flaked and packed in drums.

II PROBLEMS EXPERIENCED BY THE CHLORINE PLANT.

A: Salt handling and Resaturation section.

The salt handling system is unnecessarily complicated and the salt elevator to the resaturators, being a bucket and link type is quite unsuitable for handling such a corrosive substance as salt, which in this particular case contains much extraneous debris and is also variable in physical form.

Frequent breakdowns of this elevator create the necessity of makeshift arrangements for feeding the resaturators with disturbances to smooth running in subsequent sections of the plant.

A proposal to redesign the resaturation system to incorporate a sunken dissolving pit easily charged by mechanical shovel is supported in principle. It will be necessary, however, to establish the nature of the salt feed, available consistantly, before design can proceed with confidence. Thus although a high purity refined salt is available, this would not be suitable for this type of storage or resaturation.

B: Brine purification section

This section of the plant requires precise control of the conditions for the precipitation of all three materials, but at present calcium sulphate is not removed. This is regrettable, because although this is primarily necessary to control the sulphate content of the circulating brine, an important consequential effect is that the excess calcium chloride necessary to precipitate the moderately insoluble calcium sulphate improves the ratio of calcium to magnesium in the subsequent precipitation of calcium carbonate and magnesium hydroxide. The presence of calcium sulphate also improves the dewaterability of the sludge.

Calcium andmagnesium are precipitated by the reagents with help of a flocculating agent. Calcium carbonate forms a fairly compact particle which settles fairly well, but magnesium hydroxide forms a gelatinous floc which requires the flocculating agent to form particles which even then will settle only with difficulty. The settling of the magnesium is greatly assisted by the co-settling of the calcium carbonate and it is very desirable that the ratio of calcium to magnesium in the raw feed should be as high as possible.

It is therefore important that the ratio of calcium to magnesium impurity in the salt fed to the plant should be controlled by a tight specification of the quality of salt supplied. Some chlorine manufacturers insist on a calcium-magnesium ratio of at least 2.4:1, but this can only be achieved by skilled salt field management.

It will be appreciated from the comments above that to achieve the precisely controlled conditions necessary to produce high quality purified brine consistency of quality of the salt raw material is an important consideration.

In addition a reduction in the total impurity content is obviously desirable in the case of the mercury cell plant in order to reduce the total quantity of mercury contaminated sludge.

The suggestions made by membrane cell contractors that the sand filters would be improved by replacing the sand with crushed anthracite is supported.

C Cell room

Physical condition of the cells

The electrolysis cells are the key components of the plant and are, unfortunately, that part of the plant which has deteriorated most severely.

The cell base plates which should be scrupulously clean, smooth and free from corrosion, are heavily corroded and pitted. This condition has arisen partly because of the frequent plant shut-downs experienced (see ANNEX 1).

When a power limitation on the whole complex arises, the two plants which are thought to be capable of shutting down without damage are the polythene plant and the chlorine plant and are frequently required to do so. Mercury cell chlorine plants cannot be shut down frequently without causing serious damage, unless special measures are taken.

A mercury cell plant, although flexible for load variation over a wide range, should be shut down only if no other possibility exists. When the base plate ceases to be cathodic, corrosion will begin and, indeed, a cathodic
potential (about 1.0-1.5 volts) should continue to be maintained. This requires a small auxillary rectifier which is not available at Skikda.

However, it is also apparent that inadequate measures have been taken to protect cell base plates of idle cells. When a cell is to be taken off-load for any length of time, the anodes should be removed, the base plate cleaned and dried thoroughly and anti-corrosion measures taken. For example, in some cases, the dry base plates are covered with polythene sheet which is sealed at the edges and the air inside the the enclosure thus created is displaced with dry nitrogen. Where significant depressions in the base plate have been formed by electrode shorting, these should be ground out, filled with weld-metal and ground flush with the original surface. These extreme measures are indicative of the care with which(cedl base plates should be maintained.

Frequent plant shut-downs have also led to joints on the cells leaking mercury and chlorinated brine, because of thermal contraction of the cell causing joint strain. There may be a design weakness here. Such leaks cause much external corrosion of the plant.

The rubber lining of the cell side channels and end-boxes are failing with increasing frequency also causing spillages. With a cell room 8 years old this is to be expected and a system of scheduled maintenance is required. An inspection shows that the lining is very thin, indicating that an extensive replacement programme will be necessary before 1990, the earliest date that membrane cells could be installed.

The flexible cell covers harden and crack causing air to leak into the chlorine cell gas, diluting it, but paradoxically also causing chlorine emissions which adds to the heavy external corrosion. This is a poor design feature of this particular cell, but an improved specification of the cover is available. This incorporates a PTFE layer protecting the cell side of the neoprene sheet.

The external corrosion is most apparent on the copper flexible connections between the anodes and the cross-cell aluminium bus-bars, many of the flexibles being in a very poor state.

The many cell room shut downs should provide many opportunities for leaking joints to be repaired. It would appear that insufficient attention and forward planning is given to this.

Cell voltage

The power-driven anode adjustment system, although in principle a good design, has suffered from corrosive attack on the exposed drive mechanism and does not always operate adequately to prevent electrode short circuits causing anode and baseplate damage. The poor state of the base plates causing an uneven mercury flow exacerbates this problem. To avoid this difficulty, the cells are operated with a large electrode gap, thus performing with a high cell voltage.

At Skikda, the cells are operating with a K-factor (see ANNEX 2) of 0.37-0.40 at about half maximum amperage. The plant was designed for a K-factor of 0.14, which should be readily obtainable in cells of the type installed.

Table 1 - Cell performance

Current passed through cells, Kiloamperes		100	210	100	210
	K-factor	Cell voltage, volts		Power consumption (current efficiency 95%) KWh/t Cl	
Skikda-design	0.14	3.69	4.20	2926	3342
Skikda-present	0.37	4.46	(5.82)	3549	(4630)
Skikda-high load elcetode gap	0.20	3.90	4.63	3103	3684

At such high electrode gaps, it will be seen from the table, the cell voltage at maximum load would be very high and, indeed, cause the cells to boil, the maximum practical voltage being about 5.0 volts. It was thought by the staff of ENIP that the K-factor could be reduced at maximum load to give an average cell voltage of circa 4.6 volts. This, however, means some cells would be operating near to the 5.0 volt limit, depending upon their baseplate condition and some anode damage would probably occur.

The mission believes that it is unlikely that the plant can be operated at its maximum load with all cells operating and that the plant is no longer capable of its design load of 110t/day chlorine (about 75t/day chlorine is probably realistic).

D Chlorine handling section

Some corrosion has occured in the Hastelloy C coolers of the sulphuric acid drying towers. This is almost certainly due to the absence of a brine mist filter after the chlorine cooling towers. This is a serious design fault. It is recommended that either a Brink or Begg-Cousland Polyester fibre mist filter be installed. Failure to remove brine list at this point causes the formation of hydrochloric acid in the sulphuric acid drying towers corroding the Hastelloy C components. Furthermore, the brine mist, converted to sodium sulphate, causes sludge accumulation in the acid of the Nash compressor and even in the liquefiers.

The Nash compressors are a complex and not very reliable items of equipment and could be replaced by a radial turbo-compressor which is simpler and more efficient. A number of excellent machines of this type are now available.

Such measures would undoubted improve the reliability of this section and reduce plant interruptions.

E Chlorine liquefaction section

This section is shut down at present. This is said to be for maintenance, pressure testing of vessels, replacement of valves, etc. The use of the chlorine storage as a buffer between the chlorine plant and the VCM plant has caused problems because the VCM plant needs some oxygen in its chlorine feed and, at present there is no means of injecting this into the vapourised liquid chlorine withdrawn from stock.

There seems to be reservations about the propriety of storing large amounts of liquid chlorine, but some reduced storage would seem to be acceptable and desirable.

There is no doubt that the use of this plant and its associated storage would reduce the numbers of plant interruptions experienced by the chlorine plant.

The potential hazard for liquid or gaseous chlorine emissions can be assessed by recognised methods of hazard analysis. A reputable firm of consultants should be asked to assess the risks associated with the present installatio-. The firm Cremer and Warner (Reference 2) have a world-wide reputation in this field.

The mission were informed in a meeting at MEICIP on Jan 31, that ENIP had proposed storing VCM in two of the spheres at the same time as three/four spheres would be used for liquid chlorine storage. Surprisingly this was not mentioned to the mission at Skikda.

It would almost certainly be necessary to build a fire-wall between the two storage installations, but the storage of these two materials in such close proximity cannot be supported without a detailed hazard study.

F Anhydrous caustic soda section

This plant is shut down. The problems associated with it are not considered in detail as their only relevance to the study is that this plant was responsible for many of the plant interruptions in earlier years. Caustic soda is now distributed as 50% liquor, but the potential for this is limited and the plant will be restarted after it has been redesigned and refurbished.

III MERCURY LOSS ANALYSIS

A Mercury consumed

The amount of mercury consumed at Skikda is astounding as illustrated in the following table.

Table 2 - Mercury consumption

	1986	1987
Mercury consumed t/yr	15.10	25.88
Chlorine produced t/yr	10053	7995
Mercury consumed per t chlorine Kg/t	1.52	3.23
Mercury loss from typical European plant, Kg/t	< 0.1	< 0.1

No records are kept of mercury movement between different parts of the plant, only of amounts withdrawn from store and added to the cells. No estimates are made of the amount of mercury held in the cells. When these were commissioned 112 flasks (3.864t) were issued per cell i.e. 69.557t for the whole cell room. Procedures exist which enable moderately accurate estimates to be made of the mercury stock in the cells at any time, but these are unknown at Skikda. (see ANNEX 3)

Mercury is added to the cells, if the mercury circulation is too low. Loss of mercury may be the cause, but other possibilities may be wear or partial blockage of the pump impellor, excessive hold-up on the base plate, mercury seals, etc. All these are possible in the present state of the plant. The amount of mercury in the cells may therefore be greater than that originally charged to them. The mercury loss as estimated by the consumption data may be overstated. This cannot be confirmed until the cells are shut down and the mercury discharged and weighed.

B Loss in brine purification section

The main factor contributing to the high mercury consumption (and to a real loss) is the frequent plant interruptions. When the mercury in the cells ceases to be cathodic with the breaking of the DC current, extensive solution
of mercury in the chlorinated brine occurs. Also on cell start-up much mercury dissolvs in the brine. This problem is aggravated by the poor state of the base plate which causes turbulent mercury flow which increases solution. For these reasons the mercury content of the circulating brine can be high, giving high losses in the sludge from the brine purification section.

Snap analyses of this sludge recently indicate that the mercury content is 600 ppm Mg. These analyses were not taken at the time of plant interruption and are probably below the average level.

The quality of salt fed to the plant is consistantly much inferior to that customarily used by mercury cell plants, containing as much as 8% of impurities. This is an important factor as the volume of sludge produced is much increased.

An approximate estimate of the annual mercury loss in the brine purification sludge, taking these factors into account is about 1.3t/y.

C Loss from mercury spillage

No detailed records exist for the mercury recovered from the sumps in the cell room drainage system, but an approximate estimate is that this amounts to 750-1000 Kg/week, varying with shut down frequency because of spillage from the cells as discussed in Chapter II, Section C. General experience shows that when mercury is spilled only about some 70% is recovered as mercury is lost by vapourisation, seeping into tiny crevisses in the concrete floor etc. It is estimated, therefore, that the mercury loss from this source could be about 10t/y.

D Loss from caustic soda filtration

The caustic soda liquor before filtration contains about 10 ppm Hg in suspension. This is collected in the filter medium of the precoat filter. When the filter is cleaned, the spent medium is discharged to the waste water treatment plant where most settles in the sludge from the alum treatment thickener. This is mixed with the brine treatment sludge before dewatering.

This filter medium is rich in mercury and may contain as much as 50%. At present plant loads, it would contain about 0.5t/y Hg. As this will mix with the dewatered sludge in discrete surges, it is unlikely to have been detected in the snap samples taken.

This spent precoat should be dewatered separately and the mercury recovered from it by retorting or be taken into solution by chlorination.

E Loss from hydrogen chiller

Hydrogen leaves the cells at 35°C saturated with mercury vapour. This is chilled to 15°C with chilled water. The condensate including mercury droplets goes to the waste water treatment plant, where the mercury will mostly finish up in the dewatered sludge from the brine filtration plant. At present plant loads this amounts to 0.2t/y. This condensate should be treated separately either by recycling to the dewater feed system, if possible or by settling and either retorting the sludge or dissolving it by chlorination.

F Loss from theft

The possibility of mercury theft cannot be ignored, although no cases have been detected. Theft would be easy on this site, but perhaps disposal of the stolen mercury may be difficult, as this requires a fairly sophisticated scrap metal industry. Most mercury cell operators do have a theft loss, the scale of which is very difficult to assess.

F Summary of mercury losses

From the above sections, mercury losses can be accounted for very approximately as follows:

Brine filtration sludge	
Poor quality salt and plant interruptions	1.3t/y
Caustic soda filtration	0.5t/y
Hydrogen chiller	0.2t/y
Spillages in cell room caused by plant interruptions	10.0t/y

These estimates are of the same order of magnitude as the consumption experienced and are believed to indicate the chief sources and causes of loss.

A much more detailed and extensive investigation involving many analyses, checking of quantities and recording over a lengthy period of time would be necessary to develop anything approaching a reasonable mercury balance.

As a general comment not enough routine analyses are carried out. There is a tendency to accept the intended design analyses of various process streams as achieved fact. On a number of occasions the mission was quoted the design analyses in response to a question because actual analyses were not available.

IV MERCURY HYGIENE

It is almost universely accepted in the international community of mercury cell operators that certain standards of mercury hygiene are observed, these chiefly comprise regular tests of the atmosphere in the cell room and other potentially mercury contaminated areas (see ANNEX 4) and routine testing of exposed workers, usually for mercury in urine, but sometimes in blood.

None of these measures are applied at Skikda. It is said that some urine analyses were carried out by an outside medical laboratory some years ago and were found to be satisfactory. The apparatus for testing of mercury in the atmosphere is broken and has not been replaced. It is assumed that because three sides of the cell room are open that no high atmosphere mercury concentration will arise. This assumption is not justified, in view of the extent of the spillages observed.

V WASTE DISPOSAL

All the mercury contaminated solids ultimately appear in the dewaterd sludge from the brine purification plant belt filter. At present levels of plant output (45% design) the production rate is calculated to be 6t/day of dry solids as a cake containing about 50% water. Visually, however, this appears to be an over-estimate. No plant data is available.

Snap samples indicate the sludge to contain 600 ppm Hg, although as discussed elsewhere this may be much higher on occasion. This sludge should be sampled more frequently and a proper average sample be prepared for analysis.

The plant is in a poor state of maintenance and only one of the two filters is working. The process of extracting mercury from the sludge with hypochlorite liquor is not being used for this reason. This is regrettable. However, the present method of fixing the mercury as the sulphide is generally accepted as sound practice.

It is accepted in the U.K. and other parts of Europe that waste containing mercury may be disposed of to monitored land-fill sites. (Reference 1)

The site of the tip can be lined with an impervious clay layer or be in impervious rock or clay, but this is not regarded as essential. It is recommended that run-off water be monitored for mercury content and boreholes may be sunk to obtain water samples in the tip or in its vicinity. Experience shows that no significant mercury leaches out to ground water. Such monitoring should be carried out with the knowledge and co-operation of the local authority concerned with water affairs.

However, if a remote arid site could be found, this would simplify monitoring and give the public confidence that the mercury contamination was securely confined to the tip.

Construction debris and scrap which may be contaminated e.g. concrete rubble and steel from the conversion of mercury to membrane cells, can also be disposed to similar tipping sites.

There is a mercury mine at Azzaba, 30 kms from Skikda. It is probable the tailings from ore concentration or the residue from the mercury retorts will contain at least as much mercury as the waste from the chlorine plant. Some co-operative scheme for waste disposal should be considered.

The search for a landfill site has been made more difficult because of fears of environmental damage from such disposal sites. Such fears are unjustified as demonstrated by the operation of such sites in the U.K.

It is suggested that a consultation with the Bureau International Technique du Chlore, Brussels (Reference 1) would be useful in providing full information concerning European practice. This organisation is the society of chlorine manufacturers in Europe and has access to all practices safeguarding the environment accepted by European Governments.

VI MEMBRANE CELLS

A Description

Membrane cells use an ion selective membrane to isolate the reaction of the anolyte compartment of the cell from those of the catholyte compartment. The anodes are made of coated titanium and the cathodes usually coated nickel. Chlorine gas is generated at the anode and caustic soda and hydrogen made at the cathode. The cell requires to be fed with extremely pure brine to the anolyte and pure water to the catholyte compartment.

The brine flows through the anolyte compartment being partly depleted, but the flow is significantly less than that needed for mercury cells. Therefore, when converting from mercury to membrane cells, the brine flow around the brine resaturation and purification circuit can be considerably reduced. The reduction possible varies with the type of membrane cell.

This simplifies the preliminary brine purification, but further purification is necessary to reduce calcium and magnesium levels to less than 50 ppb. A pre-coat filter and two or three ion exchange columns are typically added.

The chlorihe cell gas contains almost no hydrogen but appreciable amounts of oxygen. Measures can be taken to control the latter to 0.5%.

The caustic soda produced is limited in strength to 35%, so additional evaporation is necessary to produce 50% liquor.

B Characteristics

The concentration of brine in the anolyte and of caustic soda in the catholyte must be controlled within fairly close limits and stringent control of purity maintained otherwise the membrane can be damaged. Depending on the type and severity of the departure from normal conditions, the membrane can be damaged such that the cell ceases to function completely. With less serious damage, loss of current efficiency results, giving higher oxygen content in cell gas and higher chlorate concentrations in the circulating brine, which can only be tolerated to a certain degree. Mercury

cells even when damaged like the cells at Skikda can continue to make chlorine although inefficiently. Membrane cells are less tolerant to damage before they cease to be able to make chlorine at all.

Although membrane cells can be switched on and off easily, it is necessary to maintain the anolyte and catholyte conditions and to apply cathodic protection. Failure to do so can damage membranes or nickel cathodes. During changes the risk of conditions becoming abnormal are greater than when operating steadily at constant level. However, given proper attention to controls, membrane cells can be taken off load more easily without damage than mercury cells. In fact some cell manufacturers suggest taking units of load as routine for certain maintenance procedures.

To ensure good control of electrolyte and, particularly, of anolyte purity membrane cell systems are equipped with a number of analysers, some such as the low calcium level analysers being very sophisticated. However, with a three tower non exchange system, it is acceptable to confine these analysers to the laboratory. Special training in their operation is required.

VII COMMENTS ON SOME MEMBRANE CELLS

A De Nora 33 DD 175 cell

This is a monopolar cell with large anolyte and catholyte compartments made with titanium and nickel coated card iron frames each being fitted with anodes and cathodes respectively. These are large structures each frame being 1.75m^2 in area, there being 15 titanium coated and 17 nickel coated frames per cell.

The large frames give the potentiality for poor current distribution as the current enters and leaves the cell from the vertical edges of the frames. De Nora has overcome this problem by having massive castings inside the frames. This is probably effective but is a very expensive construction. This problem will be greater with the 33 DD 175 cells proposed by de Nora for Skikda than with the 33 DD 88 cell installed at Cagliari because the former is twice the length horizontally.

Even current distribution is important, because areas of high current flux can cause hot spots on the membrane, which will shorten its life.

The electrolytes circulate from the top of the frames into gas separation tanks and return to the base of the frames together with feed brine or water as the case may be. The large volume of liquor in the cell forms a reserve buffer against variations in feed liquor compositions, although the mean composition in the electrolysis chambers is close to the exit composition. This permits a low brine feed rate.

The mission believes that this is a sound, but very expensive design made by a company with a good reputation in the chlorine field.

De Nora has no operating chlorine plants themselves, having to rely on customer experience, but they have an association with Dow, although Dow have not got a very high reputation in the chlorine industry for being technically advanced.

B ICI FM21 Cell

This cell was first commissioned in 1977 and was the first cell of its type, namely, a frameless cell with small electrolyte compartments comprising only the electrodes and the gaskets.

The cell is mounted horizontally with a short vertical height, current entering and leaving the cell at the top and bottom respectively, giving excellent current distribution and small gas bubble effect. There is no internal circulation and the cell therefore requires a higher brine feed rate than, for example, the de Nora or Asahi Geass cells but benefits from the higher brine strength in the cell, which is the average of inlet and exit concentration.

The small electrolyte volume also makes it respond more rapidly to feed liquor changes than the larger frame type cells, thus good control of feed liquor conditions is required.

The low vertical height gives the cell the most uniform current distribution of any cell design. The uniform current density over the membrane surface makes high average current densities possible without developing hot spots giving long membrane lives. The cell is very light and easily moved by fork lift truck and is appreciably cheaper to construct than the frame design of cell, the electrodes which are the only metal parts in contact with the electrolyte being made by pressing from titanium or nickel sheet.

ICI are the second largest chlorine manufacturer in the world, but they do not make membranes. They have extensive research facilities on membrane assessment the results of which are available to customers.

C Asahi Glass AZEC MD cell

The Asahi Glass MD cell is two monopolar cells mounted together in a bipolar arrangement and are a development of the single type M cell. The individual cells are frameless and similar to the ICI FM 21 cell. They are, however, mounted with the long axis vertical sacrificing the main attraction of ICI design. This arrangement gives poor internal current

distribution and gas bubble effect with a high concentration of chlorine at the top of the cell which can cause damage to the membrane there. The gas bubbles are used to cause a circulation between the cell and external gas separation tanks.

The bipolar linking of two cells gives some of the disadvantage of the bipolar system i.e. current by-passing the cell through the liquor passages but does shorten the current path, which is a poor feature of the single AZEC type M cell.

This design is an attempt by Asahi Glass to reduce the poor features of the single cell, but it has resulted in a rather cumbersome design.

Asahi Glass are large chlorine manufacturers, but they also produce the Flemion membrane and are not likely to give unbiased advice on membrane assessment.

D Uhde GmbH, Dortmund

The mission is less familiar with Uhde cells than the others, but believes this to be a frame design essentially similar to the de Nora cell and suspects from past experience of this company that it may be a more refined design. It should be considered because of the backing of the company by the research potential of Hoechst and, particularly, of Bayer who are joint owners. Bayer has an extensive long term research programme into various commercial membrane cells.

VIII SELECTION OF CONTRACTORS FOR MEMBRANE CELLS

Worldwide there are fourteen companies currently offering membrane cell technology, although only two companies, Dupont USA and Asahi Glass, Japan are offering membranes (see ANNEX 6).

ENIF has beem approached by TEC of Japan who offer AZEC cells from Asahi Glass and ORONZIO DE NORA Technologies (de Nora) who offer their own design of cell. Discussions have proceded with these two companies since July 1987 and have reached the stage where detailed proposals have been made. A preliminary proposal was also received from Lurgi (Friedrichsfeld) but this company withdrew their proposal at an early stage. This is a very limited number of contractors to have been consulted and some of the more reputable contractors do not seem to have been considered. ENIP apparently have considered contractors who have approached them, rather than making a positive choice of contractors who might have good technology to offer.

The only way a potential membrane cell plant operator can learn about membrane cells is to talk to contractors and companies already using membrane cells of various types, which usually means via a contractor. Therefore one should consult as many reputable contractors as practicable before making a choice of cell.

At least four companies would have constituted a reasonable short list for considering proposals and the mission recommends that an additional two companies should be considered. These are:

ICI plc, U.K., who have built more membrane cell plants outside Japan (a special case) than any other company and who have powerful research facilities for independant assessment of membranes.

Uhde of Dortmund, West Germany, who have an excellent long standing reputation as suppliers of chlorine technology and who are owned by and have the support of the powerful research of Bayer and Hoechst.

IX OPTIONS FOR RENOVATION OF CHLORINE PLANT

ENIP have taken the decision to replace the mercury by membrane cells and are well advanced discussing the conversion with two contractors. They have received proposals from both, but apparently have had no formal quotation as yet.

ENIP do not, as far as this mission is aware, seem to have seriously considered the option of restoring the existing mercury cells to their design condition. This could be done by TEC, the original cell suppliers, by providing new base plates, side channels, end boxes and refurbishing cell switches and anode bus bars.

The mission has carried out an approximate comparison of the options of converting to membrane cells or restoring the mercury cells (see ANNEX 5).

The mercury cell restoration will cost about $6 million and the membrane cell conversion $16 million. Operating costs for the latter will be about $150000/y less than the former. It should be noted, however, that $468000/y for imported membranes will be required.

It should be noted that the mercury cells can be restored without shutting down the cell unit and without significant loss of production, whereas the membrane cell conversion requires four months complete cessation of production and about fifteen months operating with only half the cells available.

However, the overall power demand by the chlorine plant will be lower for the membrane option by about 5MW. This is said to be valuable because it will enable the Complex Matieres Plastiques to be more nearly self sufficient for power, relying less on imported power from the national system which is said to be unreliable.

However, when discussing operating costs ENIP where unable to give costs of the power generated by their own power station, so it is difficult to assess the true value of this reduced power demand by the chlorine plant.

The mission believes that the economic case for the membrane cell conversion has not been made, but similar more detailed costings should be made as more accurate data become available.

To operate the mercury cells successfully will require a positive effort to improve maintenance and to conserve mercury. A solution to the problem of the disposal of the mercury contaminated waste will also have to found, although a solution to this problem will be required in any case to dispose of the waste already accumulated in the factory. The conversion to membrane cells will certainly ease these problems. The mission cannot assess the value of these advantages as compared with the extra capital and foreign exchange costs incurred.

X CONCLUSIONS

1. This mission is not convinced of either the technical or economical need to convert the mercury cells to the membrane process. There is no environmental need, but the mission cannot assess the effect of the weight of public opinion. More detailed costing of the alternatives of restoring the mercury cells to their design condition or installing membrane cells is required to establish the cost of the conversion more precisely.

As the membrane cell plant cannot be installed before late 1990, it will be necessary, in the meantime, to do extensive maintenance, particularly to replace rubber-lined components. Action to reduce mercury losses must also be initiated.

It is estimated that it will cost about $6 million to restore the cell room to its design condition, some of this money will have to be spent in any case before late 1990.

2. Experience gained in the handling of mercury cells together with the addition of cathodic protection, other anti-corrosion measures for cells when off-load, and increased maintenance generally should prevent the restored cells deteriorating in the future as they have in the past.

3. In order to ensure consideration of the best technology and in the process learn about membrane cells, the number of contractors consulted about membrane cells should be increased. It is suggested that at least four of the most prominent should be consulted i.e. two more than those already consulted.

4. The heavy mercury losses experienced at Skikda are caused by a combination of the frequent plant interruptions with insufficient management effort to prevent losses exemplified by the absence of an accounting system controlling spillage from general operations in the cell room.

The problem is exacerbated by the use of poor quality salt which increases the loss by the production of excessive quantities of mercury contaminated sludge.

5. A mercury warden with support staff and adequate authority should be appointed to emphasize all aspects of mercury conversion, namely - mercury accounting, maintaining plant and floors mercury-free, mercury recovery, waste water treatment and solid waste disposal. This group should also institute measures to bring mercury hygiene up to recognised international standards.

6. The maintenance organisation requires review. The mission wondered whether the present organisation was sufficiently flexible to take the opportunities for cell room maintenance at short notice when unplanned plant interruptions occur. The delay in replacing rubber-lined items according to a schedule based on a 5 -year life expectancy is a serious fault.

The mission recognises that part of this maintenance problem arises from the difficulties of obtaining spares. Many of these difficulties are caused by the delay created by exchange control regulations and customs examinations. Faced with these problem management become reluctant to order the necessary spare until the need is empelling. This is usually too late. Alternatively excessive spares are ordered, the plant then being trapped into continuing use of out-of-date technology e.g. the case of the flexible cell covers which cannot be replaced by known better in covers until existing stocks are used up.

7. Plant modifications to improve plant reliability are desirable. These include the installation of brine mist filters, replacement of the Nash comprises by a radial turbo compressor and restoration of the chlorine liquefaction plant and chlorine storage.

8. The waste water treatment plant is designed for removing and recovering mercury which is in solution from various waste water streams. It will not recover mercury in suspended solids which is passed into the brine purification sludge and then to waste. Thus such solids as caustic filteration spent precoat and hydrogen chiller condensate should be treated for mercury recovery before the associated water is passed to the waste water treatment plant.

9. The hypochlorite mercury extraction process for solid waste should be restarted. The mercury should be recovered both to reduce the loss to the environment, but also on economic grounds.

A land-fill site should be sought for the disposal of the solid and dumping nights secured. Discussions on collaboration with the mercury mine at Azzaba for joint disposal of wastes should be initiated.

10. The poor quality of salt available for chlorine manufacture is a serious problem which will probably be even more acute if membrane cells are operated than with mercury cells. Representations should be made to MEICIP to consider ways to improve the quality of salt produced. Although the mission has some experience in this field, this was outside the limit of the present study.

11. The accounting system at ENIP did not seem able to display operating costs easily. This contributed to a general lack of cost awareness. The comparatively crude cost comparison developed in ANNEX 5 was an unfamiliar approach and the necessary data was difficult to extract from the system. For example self-generated power costs were unobtainable and imported power costs could only be determined by consulting invoices which were difficult to interpret.

It is concluded that a review of ENIP costing procedures would be beneficial, with the objective of displaying operating cost data for various cost-centres clearly and widely to generate cost-awareness as a guide to action.

XI REFERENCES

1. Bureau International Technique du Chlore (BITC)

Avenue Louise 250 - Bte 72
B - 1050 Brussels
Belgium

2. Cremer and Warner,
140 Buckingham Palace Road,
London SW1W 9SQ.
England.

3. Waste Management Paper No. 12.
Mercury - bearing wastes.

A technical memorandum on Storage, Handling, Treatment, Disposal and Recovery of Mercury including a Code of Practise.

Department of the Environment, U.K.
Published by HMSO.

ANNEX 1

Frequency of plant interruptions.

Year	% Design Capacity achieved.	Number of plant interruptions.	Production days lost.
1979	20	10	156
80	23	10	225
81	25	17	172
82	25	19	127
83	10	27	257
84	15	19	193
85	24	48	101
86	25	10	131
87	20	10	201

NOTE Plant interruptions were mainly due to the failure of the anhydrous caustic soda plant in the earlier years, but more recently limitations both of demand and frequency of interruption are mainly due to the VCM plant and to external power failures.

ANNEX 2

Cell voltage comparison

An index for comparing cell voltage performance is the ohmic resistance of the cell and its electrical bus-bars divded cathode area of the cell. It has the dimensions of ohms/M^2 and is referred to as the K-Factor.

Thus the cell voltage is expressed by the equation.

$$V = Vo + K \frac{I}{A}$$

where V = Cell voltage

Vo = the thermodynamic electrode potentials plus over voltage. = 3.23 for mercury cells under typical conditions.

K = constant, called K - Factor, ohms/M^2

I = Current fed to the cells in kiloamperes.

A = Cathode area of cell in M^2 = 30 M^2 at Skikda.

ANNEX 3

Method of mercury accounting

A strict method of mercury accounting is essential of any control is to be maintained over the loss of mercury.

A secure store must be established into which all mercury, whether newly purchased supplies or mercury recovered from various parts of the plant should be placed and the amounts and source be recorded. All mercury issued to the plant and its destination should also be recorded.

An estimate must be made of the mercury contained in the cells, as this is by far the largest single quantity of mercury to be consider in any mercury balance. This can be done by draining the mercury from each cell when it is shut down for cleaning and weighing it. An amount must be added for the mercury remaining in the seals between different parts of the cell. (This so-called "dead weight" mercury can be measured when the cell is first commissioned) The total amount of mercury in the cell is thus determined. This amount is adjusted by adding mercury to restore the cell stock to its initial commissioning capital issue. This the loss of mercury from the cell over the period since it was commissioned (or last cleaned and mercury stock restored) can be determined and a loss per cell-day can be calculated. This procedure is repeated when each cell is cleaned and gradually an average loss per day cell-day value is established.

Therefore, at any time the stock of mercury in a cell can be estimated being equal to the commissioning stock, less the average loss per cell day times the number of days since the cell was cleaned. This the total stock in the cell room can be estimated.

Combining this figure with the stock movements in the mercury store, a total mercury stock on the site is established. Variations of this stock with time give the loss of mercury over a period, together with information as to the next probable sources of loss. The loss per cell-day index is clearly useful for assessing spillage loss.

ANNEX 3 (cont.)

It should be noted that the equipment needed for this method of estimating the cell room stock is massive. For example, the cells at Skikda hold 3.864t of mercury each. The container into which this is drained must be suitably designed to hold this mass safely and appropriate weighing machine and cranes must be available. No suitable weighing tank or weighing machine is available at Skikda.

ANNEX 4

Mercury in the workplace air (all values in Hg/M^3)

Country	Standard 8 hour average	Short term value.
U.K.	50	150
U.S.A.	50	
W.Germany	100	
Finland	50	150
Sweden	50	
Switzerland	50	
France	100	
Belgium	50	
U.S.S.R.	10	
	100 ($Hgcl_2$)	
Australia	50	
Canada	50	150

ANNEX 5

Cost comparison between mercury cell restoration and conversion to membrane cells.

Items	Mercury cells restored to design performance	Conversion to membrane cells as proposed by de Nora.
	$000	$000
Capital cost of modification. (Note 1)	6000	16000
Operating Cost per year.		
(Plant at 100% capacity for 350 days)		
Electric power at $0.0228/KWH (Note 2)	3154	2393
Mercury 10t/y at $14.23/Kg (Note 3)	142	-
Replacement of Rubber lined equipment (Note 4)	18	-
Membrane renewal 2 yr life at $750/$M^2$	-	468
Steam 0.53t/t at $18.55/t	-	430
Electrode coating renewal (Note 5)	362	335
Excess maintenance for mercury cells (Note 6)	100	-
TOTAL	3776	3626

Note 1 The capital cost of restoring the cell includes installation of new base plates, new side channels, end-boxes and reconditioning of mercury pumps and auxilliary components. It excludes all work outside the cell room.

The membrane cell conversion includes secondary brine purification and evaporation of caustic liquor to 50%.

Note 2 Cost of AC power from National system

0.03285 D/KWH	22-30 hrs to 06.00 hrs.
0.07550 D/KWH	0.600 hrs to 17.00 hrs.
0.36610 D/KWH	17.00 hrs to 21.00 hrs.
0.07550 D/KWH	21.00 hrs to 22.30 hrs.

Assuming power is consumed evenly throughout the day, average power cost is 0.1106 D/KWH = 0.0228 $/KWH.

Note 3 A loss of 10t/y is higher than would normally be acceptable.

Note 4 Assumes all rubber-lined cell parts replaced every 5 years.

Note 5 Mercury cells. 976 anodes in cell room - 2 year life.

486 anodes/y at $745/anode	$362000.

Membrane cells. 640 anodes in cell room - 6 year life.

106 anodes/y at $2356/anode	$249700.
640 cathodes in cell room - 4 year life.	
160 cathodes/y $1530/cathode	$84800.
Total electrode coating cost.	$344500.

Note 6 This is a nominal sum as impossible to estimate reasonably with data available. Illustrates higher maintenance costs of mercury cells.

ANNEX 6

Membrane cell suppliers.

Asahi Chemical Industries, Japan

Asahi Glass Co. Ltd., Japan

* Uhde GMBH., W. Germany

* Cellchem, U.S.A.

Chlorine Engineers, Japan

* Electrocell, Sweden

Hooker, U.S.A.

ICI Chemicals and Polymers, U.K

* Krebs Swiss, Switzerland

Krebskosmo, W. Germany

* Lurgi, W. Germany

Oronzio de Nora, Italy

Oxytech, U.S.A.

Tokoyama Soda, Japan.

* These membrane cells suppliers are the sole contractors for their cells. The other cell suppliers operate through a number of contractors.

ANNEX 7

Personnel met.

ENIP

Amrouche	Directeure General
Djilali	Directeure Research.

Complex de Matieres Plastiques.

Reguig	Diecteure.
Boudelaa	Dept. Chef - Technical Service Dept.
Hamouchene	Dept. Chef - Chlor - Soude, VCM, PVC
Iberaken	Chef - Chlor - Soude.
Khelaifia	Technical Service Dept.

MEICIP

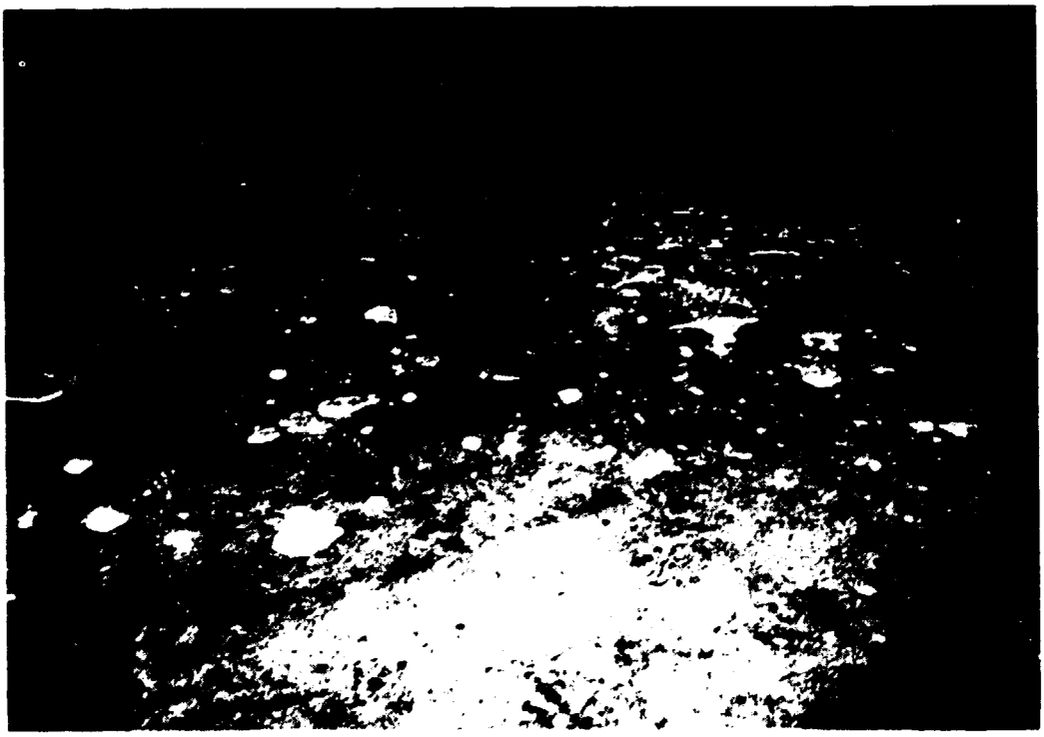
Bessam	Sous - Directeur
Djema	Ingenieur.

Photographs in cell room at Skikda

1. Corroded cell base-plate.

2. Corroded anode bus-bar flexibles.

3. Leaking chlorinated brine effluent main from cell.



4. Split mercury. Photographed 10 days after first observed in the presence of the plant manager.