HAZARDS IN THE ELECTROLYSIS OF BRINE IN MERCURY CELLS

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SUMMARY

A brief description of a typical mercury cell installation is given in order that a full appreciation of the hazards involved can be obtained. Measures which can be taken in design to overcome these dangers are indicated.

Introduction

Sodium chloride brine is a relatively harmless substance, although of course certain care must be exercised in the selection of materials of construction. However, in the electrolysis of brine, raw materials are used and products are obtained which require very careful handling. In addition to severe corrosion hazards, explosive, fire, electrical, and toxic hazards also exist, which have to be minimised by good design and careful operation. This paper has been limited to the safety measures which can be adopted by the cell designer.

The earliest type of industrial mercury cell was the famous Castner-Kellner rocking cell which started production in 1897. This was rated at 550 A. Prior to 1945, the usual operating currents were up to 14 000 A, but at the present time cells are installed which can operate up to 200 000 A. Although the same basic principles are involved, there are many different designs of mercury cell such as the horizontal, vertical, and rotating cathode cells. The hazards encountered will be generally similar for the various designs, but the following discussion will make particular reference to horizontal mercury cells.

Description of a Typical Process

The mercury cell plant at Murgatroyd's consists of two separate electrical circuits of Uhde cells, each having an anode area of 10 m^2. A common brine feed supplies all the cells, and chlorine from both cellrooms is combined into a single stream; this also applies to the hydrogen and caustic soda systems.

The principle of mercury cell operation can be explained by reference to Fig. 1. A cell consists essentially of two main units; an electrolysis cell and a decomposer. Strong brine fed into the cell is electrolysed, chlorine is liberated at the graphite anode, and sodium amalgam is formed at the mercury cathode. The sodium amalgam passes into the decomposer where it is short-circuited by graphite grids floating on the surface of the amalgam. Water is introduced in this compartment and decomposition of the amalgam occurs to produce hydrogen and caustic soda. The mercury flows by gravity along the cell and decomposer, which are slightly inclined to the horizontal. It is then lifted back to the cell inlet by a centrifugal pump.

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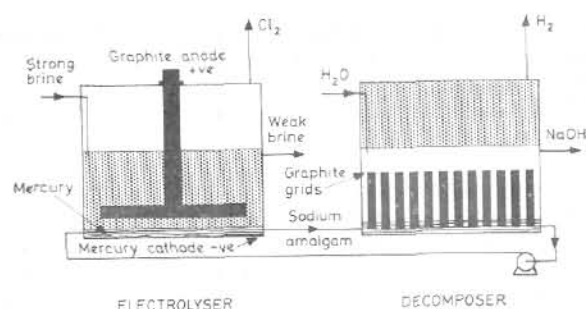

Fig. 1.—Principle of mercury cell operation

The ancillary equipment associated with an electrolytic cell plant is outlined in the simplified flow diagram shown in Fig. 2. Sodium chloride brine containing 310–315 g/l of sodium chloride enters the cells, and is depleted by electrolysis to 270–280 g/l sodium chloride. This weak brine or anolyte contains dissolved chlorine and this is substantially removed in a dechlorination unit. Solid salt is then added to resaturate the weak brine and impurities are precipitated from the brine by suitable reagents. After allowing sufficient time for the precipitation reactions to reach completion, the brine is filtered and returned to the cells. Caustic soda is collected in transfer tanks and pumped to storage. Chlorine is cooled and dried before compression, and the hydrogen is cooled, prior to internal usage or compression.

Electrical Hazards

Electricity is the principal raw material employed in the electrolysis of brine, currents from 30 000–200 000 A being used in most modern plants. Individual cell voltages are generally in the range 3·7–4·5 V, depending upon the cell design, operating current, and cell condition. The cells are connected in series and circuit voltages of about 200 V are common practice, although some mercury cellrooms on the Continent operate up to 700 V. The use of electricity on this scale presents a number of hazards.

Personal injury

With circuits at 700 V, there is a potential danger of personal injury due to electric shock. In the case of 200 V electrical circuits, the maximum potential to earth is normally
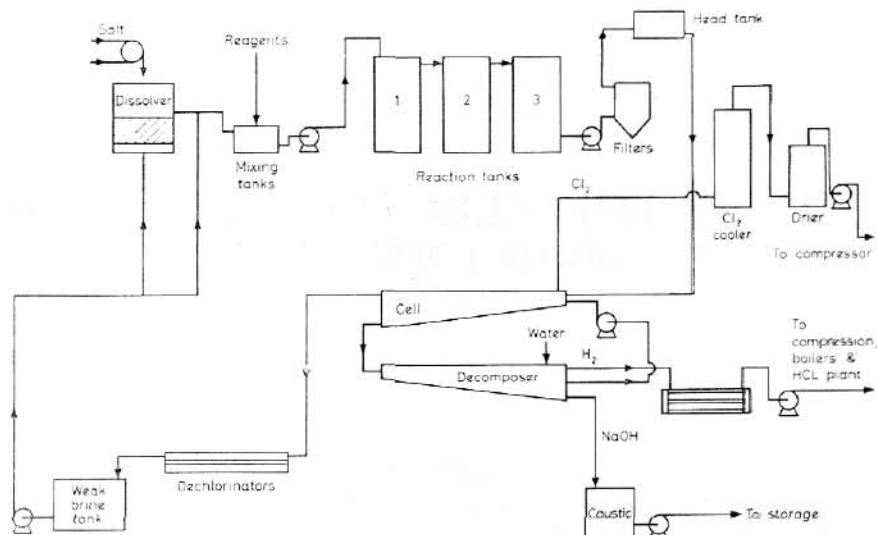
Fig. 2.—*Flow diagram of mercury cell plant*

100 V, but in the event of a fault in insulation this can increase significantly. Even when a person receives only a slight shock, indirect injury can often occur as a result of involuntary reactions. Serious burns can be caused by large amperage currents at low voltage.

Corrosion of materials

When one handles fluids such as brine and caustic soda, which are good conductors of electricity, it is inevitable that some leakage of electric current must occur, even with a well-insulated brine circuit. If insulation faults exist, the leakages will increase and severe corrosion can take place.

Fire and explosion

There is always a danger of sparking with an electrical circuit. This is particularly serious in a cell-room, in view of the presence of a hydrogen fire risk, and on occasions, of explosive mixtures of hydrogen–chlorine and hydrogen–air. Accidental earthing or faulty insulation can cause fusing of metal parts, and set fire to inflammable materials such as rubber lining.

Protection against Electrical Hazards

Safety in the design of electrical installations is controlled by the Electricity Regulations (Factories Act), but there is a special dispensation for electrolytic cell-rooms as covered in Exemption 4.

Application of the ordinary regulations would make cell-room operation extremely difficult and equipment would be extremely expensive. For example, no work should be carried out on live electrical equipment, but cells are always at a potential even when short-circuited. According to Exemption 4, it is up to the operator to take " special precautions as may be necessary to prevent danger ".

Precautions which can be taken will now be considered.

Rectification equipment

With the older type of rectification equipment, such as mercury arc rectifiers, it was necessary to operate at high voltages (500–700 V) in order to achieve efficient conversion of current. Nowadays, semi-conductor rectifiers are available which can operate efficiently at 100 V. This, coupled with the increasing tendency towards large amperage cells, has meant that high outputs can be obtained with circuit voltages below

200 V. This development has contributed greatly to increased safety in electrolytic cell-rooms.

Process equipment

The cells must be insulated from earth by mounting on porcelain insulators.

Most types of cell are provided with a set of short-circuiting switches, so that a cell can be taken out of circuit for maintenance. It is important that these switches should be well designed in order to avoid overheating and possible fires. Self-wiping contacts should be incorporated which are arranged so that the minimum of dirt can lodge on the contact surfaces. Silver contacts are often used, although various metal coatings have been tried in order to prevent the formation of corrosion products. If a set of four or more switches are installed per cell, it is advisable to design the switches with a safety factor, since cell operating conditions can cause uneven current distribution through the various sets of busbars.

In order to reduce earth leakage and consequent corrosion to a minimum, it is necessary either to completely break the liquor streams connected to the cell or to insulate the pipework. Current breakers are often employed on the caustic soda leaving the cell, but it is a difficult proposition with the brine stream because of the large flow involved. It is generally considered that the most effective method is to insulate the pipework from earth.

The pipelines attached to the cells are supported on insulated hangers and every pipe section is insulated from its neighbour by non-conducting ferrules fitted in the flange bolt holes. This applies even to rubber-lined pipework, since it avoids a complete pipeline becoming alive, if for any reason the rubber lining should fail on one section. Any service lines, such as compressed air, near to the cells should incorporate a rubber section to break the path to earth. In some cell-rooms an attempt is made to control the leakage path by installing a graphite rod in the weak brine circuit, and thereby making a deliberate earth. Another method is to install a " sacrificial " section of pipe which is deliberately earthed in order to prevent corrosion at more vital points.

The pipeline insulation should be good enough to ensure a total minimum resistance to earth of 3–10 ohms when the circuit is in operation.

Any electrical tools or instruments used in the cell-room should have a separate low voltage supply which is insulated from earth. The mercury-pump motors are fed with a

separate supply which is also insulated from earth. In the event of a failure of this power supply, there is an interlock which automatically trips the rectification equipment and minimises the danger of explosion in the cells.

It is recommended that cranes used in the cell-room should be doubly insulated from earth by insulating the crane hook and the traverse rails. Instruments such as pH meters which are connected to the brine main should not be earthed, otherwise the brine pipe will become earthed. A mid-point voltmeter can be installed to give warning of any earth faults which may occur.

Even with a well-insulated electrical circuit, cell-room floors are often covered with a non-conducting material such as asphalt, to provide an additional safeguard. However, some cell-rooms on the Continent operate at high circuit voltages with concrete floors. The floors should be well drained so that water or brine cannot lie in pools. Steel stanchions within reach of the cells should be clad with an insulating material.

In spite of all the design precautions, operators in high-voltage cell-rooms should be equipped with rubber boots and gloves which are regularly tested.

Toxic Hazards

The toxic hazards encountered in mercury-cell operation are those due to mercury, chlorine, barium, and lead. Barium carbonate is used for the purification of brine and a lead alloy is handled in the cell-room workshops during anode assembly. These operations are less extensive, and the precautions to be taken are generally well known. The following discussion is therefore restricted to the two main hazards of mercury and chlorine.

Mercury

Depending upon cell size and design, mercury cells can contain up to four tons of mercury. For a modern cell-room producing 100 tons of chlorine per day, the total mercury requirement may be as much as 100 tons.

Mercury is well known as a poison and it is absorbed through the skin or inhaled as a vapour. The generally accepted figure for the maximum allowable concentration of mercury in the atmosphere is 0.1 mg/m^3. This is the American standard and it is also used on the Continent, although one notable exception is the USSR, where the limit is reported to be 0.01 mg/m^3, in a recent paper.[1]

Mercury is slightly volatile at room temperature and will be present in the atmosphere when metallic mercury is handled in the open. The mercury concentration of the atmosphere increases rapidly with increasing temperature (see Fig. 3). Temperatures up to 85°C in the cell and 120°C in the decomposer are experienced, causing a considerable amount of heat to be dissipated into the cell-room atmosphere. Exposed mercury surfaces will result in an increase in the mercury content of the atmosphere, especially if in contact with a hot surface, *e.g.* cell cover.

Frequent medical checks of cell-room personnel are carried out in order to detect any initial symptoms of mercury poisoning. In order to achieve a low mercury content in the atmosphere, it is necessary to combine safeguards in design with a high standard of housekeeping. The Draft Mercury Process Regulations 1962 quote :[2]

" Every mercury process shall be so conducted, and all plant apparatus and equipment shall be so designed, as to restrict as far as is reasonably practicable the extent to which persons employed are exposed to mercury or mercurial compounds."

The following points should be noted in the design of a mercury cell-room installation.
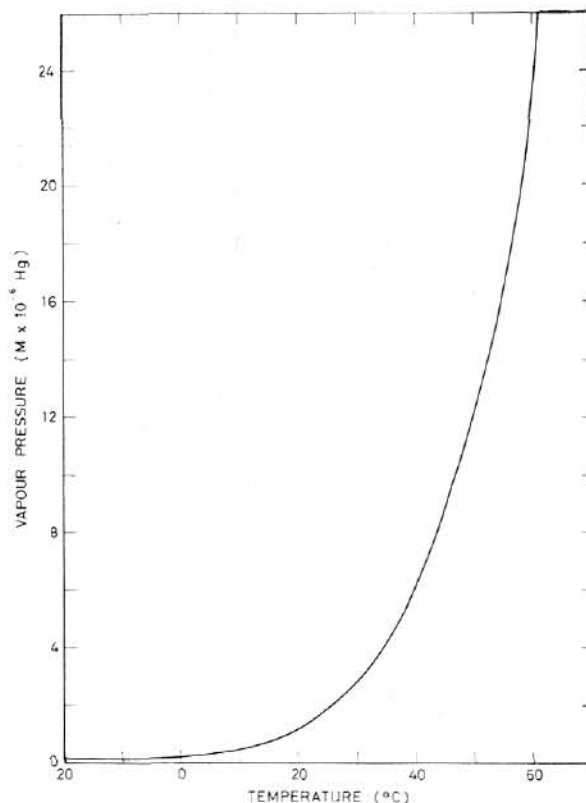

Fig. 3.—*Vapour pressure of mercury*

CELL-ROOM BUILDING

Adequate ventilation should be provided so that the large quantity of heat from the cells does not lead to excessive cell-room temperatures. Various figures are quoted for the number of air changes required per hour, and for the Udhe cell 20 changes per hour are recommended. Natural convection is often quite adequate, but in some installations it is necessary to have a forced ventilation system. Care should be taken to avoid any " dead " pockets which can become heavily contaminated with mercury.

Materials of construction, such as timber, which absorb mercury should be avoided as far as possible.

All the cell-room floors should be finished with a smooth surface so that spilled mercury can be recovered easily. A vacuum cleaner can be used for this purpose.

PROCESS EQUIPMENT

The cell should be designed so that exposed surfaces of mercury are always covered by a liquid, and close-fitting covers should be fitted where access to the cell is required. A high concentration of mercury vapour usually exists in the pump casing and this should be maintained under a suction.

Hydrogen leaving the cells contains mercury vapour and the pipes should slope continuously to mercury traps. It is important to avoid any dips in which mercury could collect, and care should be taken in making any flange joints to ensure that the inner edge of the gasket fits flush with the inside of the pipe.

When welding is necessary to any pipe which passes hydrogen, the pipe should be thoroughly cleaned initially and self-contained breathing apparatus should be worn by the welding crew. This is necessary since mild steel absorbs mercury and although a pipe may appear to be clean, mercury vapour will be released on heating.

SECOND SYMPOSIUM ON CHEMICAL PROCESS HAZARDS (1963: INSTN CHEM. ENGRS)

In most cell-rooms the combined hydrogen stream from the individual cells is cooled in a single unit. A considerable quantity of mercury is therefore recovered from the mercury traps installed in the hydrogen system. This involves additional handling which is undesirable in view of the toxic hazard. This has been overcome in at least one design of cell by installing individual coolers on each of the hydrogen lines from the decomposers. By this means, the majority of the mercury is condensed from the hydrogen and returned to the cell, thus avoiding excessive handling.

It has been found that mercury can be detected in the atmosphere above circulating brine surfaces, and in particular above *caustic soda liquor which can entrain hydrogen. The* vapour being released from hot caustic soda in the collection tanks was found to contain as much as 0.7 mg/m^3 mercury and it was necessary to connect the tank into a vent system. Any tanks therefore in which a vapour with high mercury content is likely to be present should be vented with care.

It is essential to have mercury detection equipment in order to carry out regular checks of the mercury content of the cell-room atmosphere, and thereby discover any abnormalities.

Chlorine

Chlorine is a severe respiratory irritant, and concentrations as low as 3–5 ppm (by volume) in air are readily detectable by smell. Large concentrations can cause irritation of the mucous membrane, the respiratory system and the skin. Suffocation will occur if the duration of exposure is excessive.

PROCESS EQUIPMENT

In view of the toxic nature of chlorine, it is obvious that the cell-room designer must take every precaution to ensure that the gas is not released to the atmosphere.

In normal operation, the pressure of the chlorine in the cell is usually controlled automatically at about atmospheric pressure. A suction applied to the brine-seal chamber at the end of the cell avoids excessive smell from the chlorinated brine. With most types of cell it is necessary to remove the chlorine contained in the gas space when the cell is taken off work for cleaning. The following measures can be adopted to avoid escape of chlorine into atmosphere when it is being vented :

Discharge the gas into a dilute gas main for subsequent absorption.

Use a small extraction fan and absorber fitted on a trolley.

Purge the chlorine into the chlorine main by blowing nitrogen into the cell.

Cells are usually designed so that the brine seal is broken if the chlorine pressure in the cell exceeds 4–5 in. wg because of the failure of chlorine fans or compressors. This can cause a severe escape of chlorine into the cell-room. Some cell installations are equipped with an absorption system which is capable of handling the full cell-room production for a few minutes, but such absorption systems have to be of very large capacity. In the event of a chlorine escape, respirators are maintained at strategic points although it should be remembered that the cannister-type masks are only suitable for chlorine concentrations of less than 1%. For higher concentrations, self-contained breathing apparatus should be used. Sufficient cell-room exits should be provided, so that the cell-room can be readily evacuated in the event of a serious escape of gas.

Corrosive Hazard

The corrosion caused by stray current losses from the main electrical circuit has already been mentioned, but general corrosion problems also exist. The most troublesome of these

are because of chlorine, chlorinated brine, and caustic soda, and the conditions under which they have to be handled will be considered.

Chlorine

Chlorine is produced in the cells at temperatures up to 85°C and it is substantially saturated with water vapour. Hot, wet chlorine is highly corrosive to nearly all metals, titanium being a notable exception. A comparison of titanium with several other metals is given in Table I. However, it should be remembered that titanium is not suitable for chlorine containing less than 0.015% water by weight, since spontaneous *ignition can take place. Recent investigations have also* shown that crevices should be avoided in any equipment made from titanium and designed for use with wet chlorine, since corrosion may occur.[4] This corrosion is thought to be because of the normally imperceptible reaction between titanium and wet chlorine proceeding slowly, and eventually drying out the pockets of gas.

TABLE I.—*67-Day Test of Selected Materials of Construction in Wet Chlorine at 77°C (Ref. 3)*

Metal	Corrosion Rate
Titanium	0.1 mils/year
Zirconium	90.0 mils/year
Hastelloy C.. ..	0.8 mils/year
Chlorimet 3 ..	11.0 mils/year

Natural rubber reacts with wet chlorine and a protective skin is formed. If the rubber is soft, the chlorinated product, which is brittle, adheres to the unreacted rubber underneath. Semi-hard and hard rubber react more slowly, but the chlorinated rubber is more easily removed and such rubbers are not suitable for application under conditions of abrasion. Certain modified phenolic resins and ceramic materials also possess resistance to wet chlorine. Materials of construction for cell-room equipment handling wet chlorine are detailed below.

Cell covers are often made of rubber-lined mild steel. The rubber is usually heavily graphitised in order to provide the maximum resistance to chlorine attack. One design of cell employs a hard rubber cover which only lasts for the life of a set of anodes. Stoneware cell covers have also been used.

Rubber-lined mild steel pipework is used extensively but other suitable materials are glass, stoneware, p.v.c. reinforced fibre-glass, and phenolic resins with suitable fillers.

Titanium, although still a relatively expensive material, is finding increasing application in wet chlorine systems, and a number of fans, coolers, and titanium-lined pipelines are in operation.

The instruments in a cell-room are usually contained in a pressurised cubicle to prevent corrosion by the cell-room atmosphere. None of the plant fluids are piped into this cubicle, since any leakages could cause considerable damage.

Chlorinated brine

After electrolysis, the depleted brine containing 270–280 g/l sodium chloride leaves the cells with a pH of 2.0–2.5. It is saturated with chlorine at 80–85°C, and is extremely

TABLE II.—*Corrosion Data for Various Metals in 20% NaCl Solution Saturated with Chlorine at 88°C (Ref. 3)*

Metal	28-days test Corrosion Rate	
Titanium	0.02	mils/year
Zirconium	29	mils/year
Hastelloy C.. ..	44	mils/year
Chlorimet 3 ..	156	mils/year

corrosive. Titanium is the most suitable material of construction for these conditions. Corrosion data for various metals exposed to 20% sodium chloride solution, saturated with chlorine at 88°C, are given in Table II.

The following materials are suitable for equipment handling chlorinated brine.

The cell side-walls are usually made of rubber-lined mild steel, although graphite linings are also used. The cell bottoms do not come into contact with the chlorinated brine unless the mercury flow fails. Steel bottoms are often employed, but some cell designs incorporate rubber, stoneware, or plastic covered bases. In cells with protected bases, the current is distributed through metal strips which are slightly recessed below the level of the cell bottom.

Most cell-room installations have rubber-lined mild steel pipework for chlorinated brine, although Haveg has been used successfully. Recently an 18 in. diameter anolyte main of glass fibre reinforced polyester resin has been installed in an American plant.

Rubber-lined pumps are in common use in brine circuits, although titanium-lined pumps are becoming an attractive proposition.

Sodium hydroxide

Caustic soda liquor is obtained from the cells at temperatures up to 100°C and normally containing 50% caustic soda. Rubber-lined mild steel or nickel is suitable for handling caustic soda under these conditions. Although mild steel is quite satisfactory up to 60°C, above this temperature there is danger of stress corrosion taking place. The iron content of caustic soda is of importance for certain applications, and this is noted in the design of equipment.

Decomposers are generally made of mild steel which is protected to a large extent by amalgamation. In certain cells a rubber-lined decomposer is used which will minimise iron pick-up.

Nickel is the common material of construction for pumps. If caustic soda is pumped directly to storage without cooling, it is necessary to have rubber-lined storage tanks. A nickel heat exchanger is often installed to cool the caustic to 40–45°C, at which temperature unlined storage vessels can be used.

Explosion Hazard

Hydrogen-chlorine

It is well known that explosions can occur between hydrogen and chlorine over a wide range of concentrations. In mercury-cell operation, some hydrogen is produced in the cell and although the concentration is usually small, it can rise into the explosive range. The generally accepted lower limit for an explosion is about 4% hydrogen in chlorine. In practice, the hydrogen content of chlorine in horizontal mercury cells is usually below 1·0% depending upon the cell design and operation conditions. In a well-operated cell-room, it can be under 0·2%. For an explosion to occur in a cell it is necessary that there should be an explosive mixture of hydrogen and chlorine and a source of initiation.

FORMATION OF EXPLOSIVE MIXTURES

There are a number of operational reasons for a high concentration of hydrogen in the anode compartment, but these should be avoided by good operation. It is proposed to limit this discussion to the design features which can cause increased hydrogen formation.

Exposure of Cell Bottom. If the mercury flow fails in cells with steel bottoms, the exposed bottom acts as a cathode at which excessive hydrogen evolution occurs. This danger can

be minimised by installing visual and audible alarms. In addition to warnings, failure of the mercury flow can be arranged to actuate the cell short-circuiting switches, and thereby cut the cell out of the circuit.

In cells fitted with protected bases, pools of mercury are formed over the recessed metal cathode strips. Rapid hydrogen evolution still occurs, since the sodium content of the mercury remaining in the cell increases rapidly as a result of the high current density.

Sodium-Amalgam Concentration. If the concentration of sodium amalgam into the cell increases significantly, hydrogen will be formed. It is therefore of prime importance that the cell designer should provide a decomposer which will operate efficiently at the maximum amperage of the cells. Many factors affect the performance, including slope of cell and decomposer, design of graphite grid, and the quality of the brine and feed water.

Metal impurities. The presence of certain metals such as vanadium, molybdenum, chromium, or cobalt, will lower the hydrogen over-voltage in the cell, and cause a discharge of hydrogen. The presence of such metals must be kept to a minimum, both in the graphite anodes and in the circulating brine. It is interesting to note that increased hydrogen evolution occurred on a plant, when erosion of stainless steel brine pumps caused metal fragments to be carried into the cells.

Monitoring. A hydrogen-in-chlorine instrument should be installed, to continuously record the hydrogen content of the combined chlorine stream from the cells, in order to quickly detect any marked increases.

SOURCES OF INITIATION

The following sources of initiation for explosive hydrogen-chlorine mixtures have been suggested :

mercury oxide,

nitrogen trichloride,

photochemical initiation,

sparks formed by short-circuiting or stray current leakage, and

hot spots.

In cell design, the possibility of photochemical initiation by strong sunlight should be remembered and chlorine pipes made of glass are usually coloured. Manometers, sample points, and brine sight glasses are often constructed in glass. The anode assemblies should be designed so that there is little danger of sparks because of faulty electrical contacts. Rubber-lined cell covers should be spark tested to avoid the danger of porous rubber causing sparking because of stray current losses.

Cells are usually provided with brine seals which blow in the event of an explosion.

The risk of an explosion is fairly high when a cell is switched on containing an explosive mixture. It is, therefore, desirable to arrange a vent system so that the cell can be purged before switching on.

Hydrogen-air

In normal operation, the greatest risk is the result of the leakage of hydrogen from the system and possible subsequent fires. When a decomposer is off work, it is possible to get an explosive mixture of hydrogen and air in the decomposer on start-up, and an explosion could occur if means of initiation were present.

Hydrogen systems are designed to work under a slight pressure so that leakage of air into the hydrogen is avoided. At Murgatroyd's, the pressure of hydrogen is automatically controlled, and if it should fall below 0·4 in. wg at the booster

suction, an automatic vent opens and the hydrogen is discharged to atmosphere at high level. Also, the oxygen content of the hydrogen is continuously recorded, and if this exceeds 1% the booster trips, and visual and aural alarms are operated.

Nitrogen purge points are fitted to the pipework which carries hydrogen so that the system can be purged of air before starting up the cells.

The main source of ignition of hydrogen fires or explosions is from electric sparks, and measures to avoid these have been discussed in an earlier section. Naked flames should, of course, be prohibited in the vicinity of the cell-room.

Conclusion

It is apparent that cell-room designers can and indeed do take many precautions against the potential hazards of mercury cell operation. However, it must be stressed that safety measures in design are only effective if combined with safe operation.

References

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