EXPLOSION HAZARDS OF CHLORINE DRYING TOWERS

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Summary

Three chlorine drying towers made of PVC exploded suddenly and violently in a mercury amalgam cell chlorine plant. Because of failure of the electrical power system, a current breaker tripped out, the mercury pumps stopped and the steel bottom plates in the cells became exposed. The alarm did not work, since both the AC power supply to the mercury pumps and that for the alarm system were taken from the same source. Meanwhile, the DC power and brine supply to the cells were not interrupted. Therefore, the hydrogen generated at the steel plate cathode and oxygen at the anode at a mole ratio of 4:1, forming an explosive gas mixture, passed to the chlorine drying towers.

Concentrated sulphuric acid is used to irrigate the towers for drying of the wet chlorine gas. The most likely source of ignition in the towers was the discharge spark from an electrostatic charge caused by sulphuric acid drip. The actual electrostatic charge of a PVC-made chlorine drying tower was then measured. A static potential of minus 5 kV was constantly detected near the hole which was drilled in the side wall of the space below the Raschig ring layer.

The main conclusion obtained from the studies is that the towers should be constructed of an acidproof and conductive material in the future, so that the towers can be held at the earth potential, together with sulphuric acid, to prevent electrostatically charging.

Introduction

At 3.45 p.m. on July 18, 1975, three chlorine drying towers in a mercury amalgam cell chlorine plant (Ryohnichi Co., Ltd. near Okayama) exploded. One operator was killed and twelve seriously injured.

The electrolytic chlorine process involves an inherent explosion hazard because hydrogen as well as chlorine or oxygen can be simultaneously produced and mixed in the cells. Under normal operating conditions this cannot happen. However, explosions are caused by an improper operation or maintenance or a lack of safety controls on the cells and the associated equipment.

Chlorine drying towers constructed of ceramic materials or polyvinylchloride resin (hereinafter referred to as PVC), are exceedingly susceptible to damage by explosions because of their brittle nature. Such explosions have been experienced hitherto in large numbers in this process throughout the world.
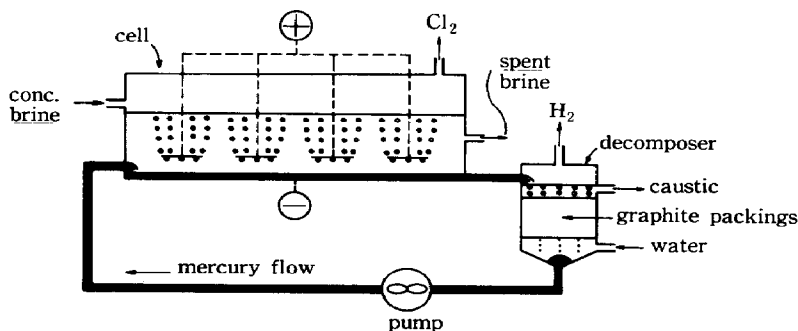
Fig. 1. Outline of structure and function of mercury amalgam cell and decomposer.

The process technology has been continuously improved based on best experiences, but nevertheless, accidents of this kind have been difficult to eliminate until now.

Description of the process and plant

A mercury amalgam cell, as shown in Fig. 1, is a rectangular steel vessel lined with rubber or other inert material, in which mercury as cathode flows down the bottom steel plate and the anode, made of graphite or some other metals, is set above the mercury layer completely submerged in brine. The decomposer is usually a cylindrical steel vessel packed with graphite particles which are held in place between screens.

In operation, mercury and brine flow into one end of the cell. Chlorine evolved at the anodes, rises through the brine and passes out through the chlorine outlet. The chlorine outlet of each cell is connected to a chlorine header pipe operated under a slight vacuum where the gas collects. Then the gas enters the water cooler and flows through the mist separator into the chlorine drying towers. The sodium formed at the mercury cathode reacts with the mercury to form amalgam. The amalgam flows to the top of the decomposer descending countercurrently to water, which is pumped into the bottom of the decomposer, to form mercury, hydrogen and caustic soda. Hydrogen and caustic soda are removed through separate outlets. The regenerated mercury is pumped back to the end of the cell.

Should hydrogen be generated in the mercury amalgam cells, it would naturally enter the chlorine line. The following situations are known to be typical cases which bring about abnormal generation of hydrogen in the cell:

(1) Should mercury supply be interrupted by the failure of the mercury pump or by a blockage of the mercury pipe, the steel bottom plate would be exposed. In that case, hydrogen instead of sodium would begin to generate at the cathode.

(2) Should ions of metals such as Cr, V, Mo, Al or Mg be present in the
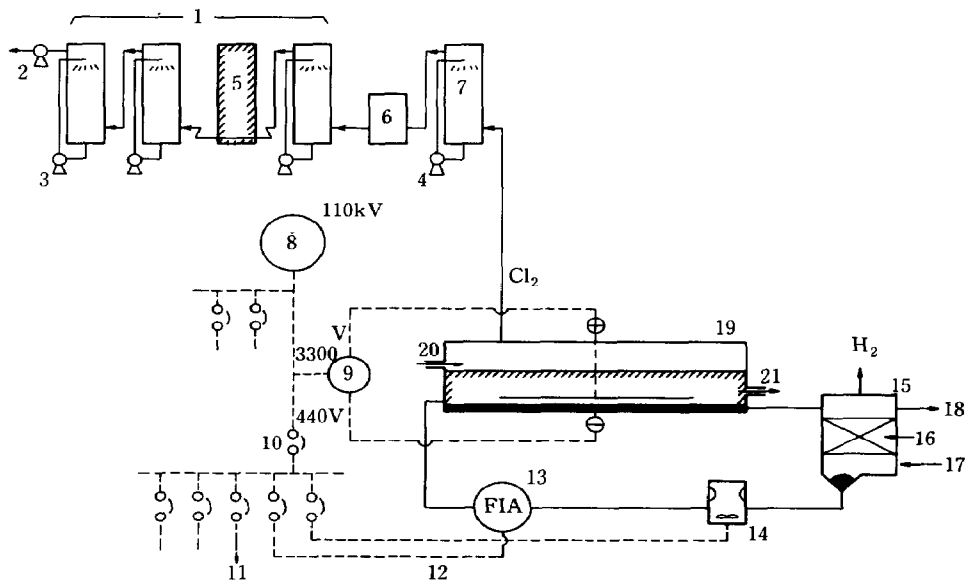
Fig. 2. Flowsheet of the mercury amalgam cell chlorine plant where the accident occurred. Key: 1, chlorine drying tower chain; 2, turboblower; 3, sulphuric acid pump; 4, water pump; 5, the 2nd tower, being under repairs; 6, mist separator; 7, cooler; 8, AC main power source; 9, rectifier; 10, no-fuse-breaker; 11, supply to an air dechlorination blower; 12, cell control and alarm system; 13, indicator and alarm for the flow state of mercury; 14, mercury pump; 15, decomposer; 16, graphite packings layer; 17, water inlet; 18, caustic outlet; 19, mercury amalgam cell; 20, concentrated brine inlet; 21, spent brine outlet.

brine, they would precipitate on the mercury surface during electrolysis. Hydrogen would be generated at such spots because it does not require such a high overvoltage as mercury surface [1].

(3) Should the DC power supply to the cells be cut off when the mercury circulation continues, the amalgam decomposition reaction would commence immediately in the cell to form hydrogen.

Flowsheet of the plant where the accident occurred is shown in Fig. 2. The main process variables immediately before the accident were as follows:

Number of cells, 37 (each 10 m × 2 m × 0.3 m high); DC current, 205 kA; concentrated brine, NaCl 290 g/l, 78°C, 450 m³/h; spent brine, NaCl 257 g/l, 85°C, 445 m³/h; mercury, 120 l/min·cell; chlorine, 3069 Nm³/h, 80°C; hydrogen concentration in the chlorine, 0.1–0.2 vol%; chlorine gas flow rate in pipe line, ca. 5 m/s.

The second drying tower was under repair, so that the chlorine pipe was connected from the first to the third tower, bypassing the second.

The feature of this plant arrangement will be seen in the flowsheet. Input to the rectifier was taken from the AC main power source. Both the AC power

supply for the mercury pumps and that for the FIAs, which were installed to check the flow state of mercury, were taken from the load side of a no-fuse-breaker rated at 600 A (hereinafter referred to as the breaker indicated as 10 in Fig. 2). The system was, therefore, in such conditions that should the breaker trip for any reason, not only would the mercury pumps stop, but also the pump failure alarms would not work.

Description of the accident

It was at the height of summer at about 3 p.m. when the highest temperature of 32.8°C was recorded at the Okayama meteorological observatory since the beginning of that year. The process variables were all kept within the set ranges at 3.30, as established by the inspection after the accident from the chart-strip recordings. At about 3.38 an operator, who was on duty at his post in the main control room, noticed that the DC current dropped suddenly from the set value of 205 to 195 kA. As the result, the shift foreman asked the operator, who was on duty in the sub-control room, situated beside the cell room, whether or not any abnormality had occurred around the cells. The operator replied by telephone "there is no specially abnormal situation". Judging from the facts established after the accident, however, there must have been some clearly abnormal state which should have been noticed by the operator. At about 3.40, that is, one or two minutes later, the DC current was restored to the original value of 205 kA by the automatic function of the current stabiliser installed on the rectifier. Although the operators in the main control room felt relieved for that matter, they then noticed that the hydrogen discharge pressure was decreasing from the set value of 0.34 to below 0.2 kgf/cm^2 (gauge pressure). The foreman instructed the operator in the sub-control room to check again the cells when the operator reported by telephone "all AC power supplies for mercury pumps and those for RICAs have been cut off!". Suspecting that some serious events were occurring in the plant, the foreman decided to carry out an emergency shutdown. Shortly afterwards, at 3.45, a violent explosion occurred in the chlorine drying towers. Three towers were completely destroyed, except for the bottom structures which were made of steel. Piping and Raschig rings in the towers, both made of PVC, were also ruptured and dispersed, some fragments being blown away up to 100 m (Fig. 3). Window glas in the plant was broken within 50 m. One operator was killed due to pulmonary edema and twelve seriously injured. They were all engaged in the repair work on the second tower.

Facts established after the accident

The position at the time of the accident is shown in Fig. 4.
The breaker tripped and when the mercury pumps stopped the alarm did not work since the AC power supply for FIAs was also cut off and so the operators
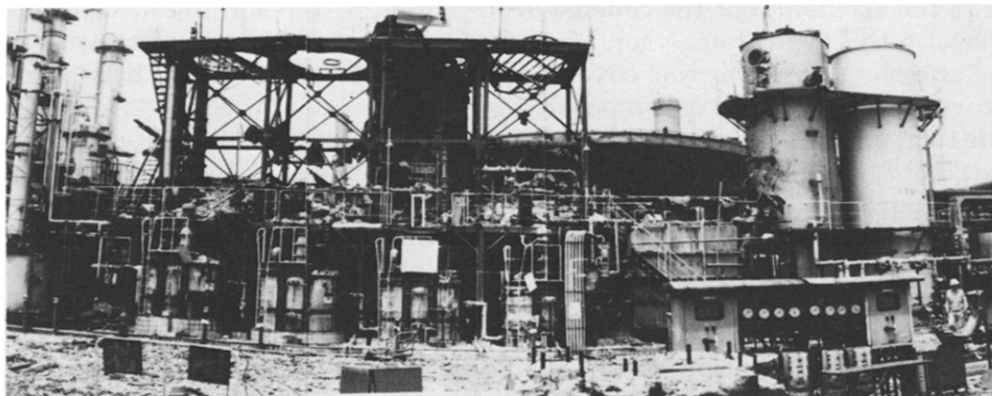
Fig. 3. The scene after the accident.

were not aware of the dangerous situation occurring in the plant. The DC power supply to the electrolytic process was on. Brine supply to the cells was not interrupted because of a separate AC power supply until the emergency shut-down immediately after the accident. Inspection of the continuous hydrogen analyser recordings revealed that the hydrogen concentration was 0.3 vol% just
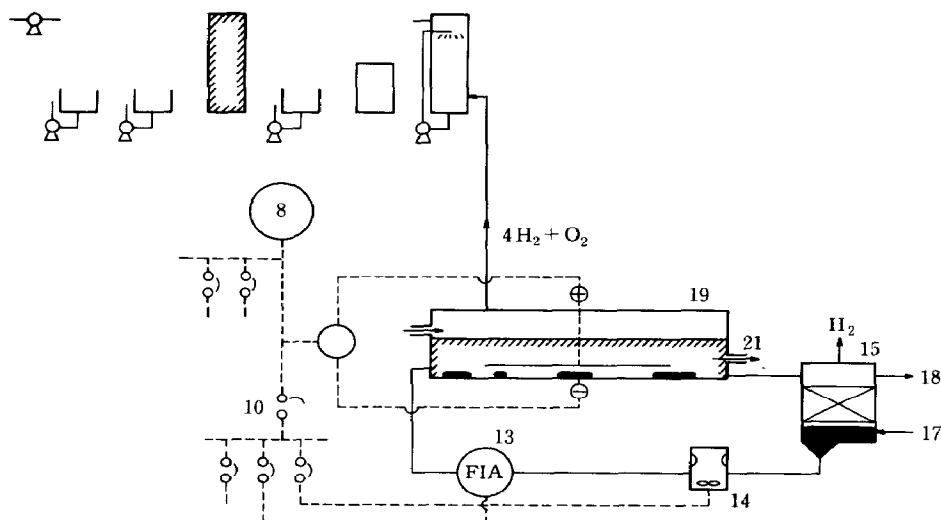

Fig. 4. The position at the time of the accident. Flowsheet and numbering correspond to those of Fig. 2. Key: 8, gross power consumption increased by about 8 MW; 10, breaker tripped out; 13, alarm for mercury flow did not work; 14, mercury pump stopped; 15, the bulk of mercury drained into the decomposer; 17, flow rate of water lowered; 18, flow rate of hydrogen and caustic lowered; 19, steel bottom plate was exposed and a part of mercury remained; 21, temperature of spent brine rose to about 100°C.

prior to the accident, but the time lag from sampling to recording was considerable with this type of analyser. Some 20% of the steel bottom plate was exposed and the remainder was covered with a thin mercury film. The bulk of mercury drained into the decomposer.

The temperature of the spent brine rose to about $100\,°C$ immediately before the accident, while its usual value was approximately $85\,°C$. In the meantime, the gross power consumption of this factory increased to about 40 MW for 5–7 min before the accident, while its usual value was approximately 32 MW. The increment of 8 MW could be explained as follows: 37 cells $\times$ 205 kA $\times$ 1 V $\cong$ 8 MW, if it is assumed that there was an increase of about 1 V across each cell due to some increase in distance between electrodes accompanied by the outflow of mercury. In addition, the unusual rise in temperature of the spent brine could also be calculated, assuming that the energy increment of 8 MW would have been converted to heat ultimately.

The probable course leading to the accident

As the breaker tripped out, the mercury pumps stopped and mercury drained to the decomposer exposing the steel bottom plate. Both the DC power and the brine supply were operating, so that some abnormal electrolytic reaction commenced in the cells. An explosive gas mixture was generated and it passed via the chlorine header pipe to the chlorine drying towers where it found some ignition source resulting in the explosion of the towers.

Factors which affected the tripping of the breaker

Detailed inspection revealed that there was no evidence of an excess current in the cables, such as could be caused by a short-circuit. A test showed that the capacity of the breaker was normal. There was no problem with the mercury pumps.

The gross load current on the breaker at the time of the accident was about 530 A because an air dechlorination blower consuming ca. 40 A was temporarily in operation on that day. The normal load current was about 490 A. Incidentally, the capacity of the breaker falls when the ambient temperature rises (Fig. 5). According to Fig. 5, should the ambient temperature reach $50\,°C$, the gross load current of 530 A would have attained to cut-off level of the breaker. The switch room, where the breaker was located, was a single-store room made of reinforced concrete and was situated alongside the plant building exposed directly to the afternoon sun. Furthermore, the switch room contained additional 325 breakers, so that the temperature inside would have been further increased by the heat generated from these electrical appliances. Thus, it was presumed that high ambient temperature was responsible for the breaker to trip out eventually.
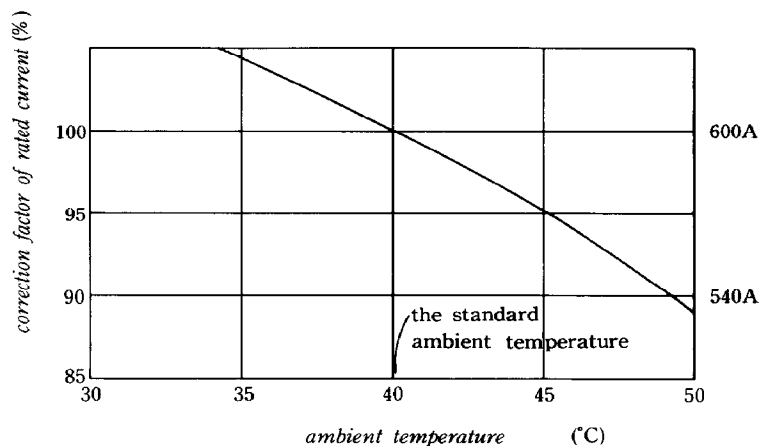
Fig. 5. Effect of ambient temperature on the capacity of the breaker.

Explosive gas mixture, if any, and its formation mechanism

On the basis of the standard hydrogen electrode, the likely reactions which might occur on the exposed steel bottom plate or on the remaining thin mercury film and their corresponding cathode potentials are shown in Fig. 6. Although the normal cathode reaction is C in Fig. 6, hydrogen would begin to generate at once on the exposed steel cathode because of its lower reduction potential [eqns. A in Fig. 6 and (1)]. The remaining mercury film would be saturated with sodium within one minute, changing into a butter-like substance. Similarly, hydrogen would begin to generate on its surface according to eqn. B in Fig. 6. Meanwhile, at the anode the successive stages of the reaction would eventually lead to the generation of oxygen according to eqns. (2), (3) and (4). On balance, hydrogen and oxygen would be formed at a theoretical mole ratio of 4:1 under the abnormal situations in the cells.
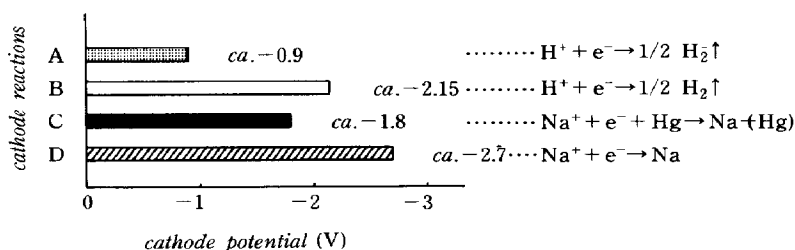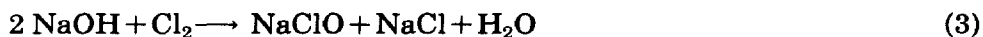

Fig. 6. Cathode reactions and their corresponding electrode potentials: A, hydrogen formation on iron plate; B, hydrogen formation on saturated Na-amalgam; C, reduction and amalgamation of sodium ion; D, deposition of metallic sodium.

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TABLE I

Results of simulative electrolytic experiments with a beaker

Cathode	Composition of gas evolved (vol%)	
Steel plate	H_2	85.15
	O_2	14.70
	Cl_2	0.12
Saturated Na-amalgam	H_2	87.66
	O_2	12.20
	Cl_2	0.11

$$H^+ + e^- \longrightarrow 1/2\ H_2 \tag{1}$$

$$Na^+ + OH^- \longrightarrow NaOH \tag{2}$$

$$2\ NaOH + Cl_2 \longrightarrow NaClO + NaCl + H_2O \tag{3}$$

$$6\ NaClO + 3\ H_2O \longrightarrow 2\ NaClO_3 + 4\ NaCl + 3/2\ O_2 + 6\ H^+ + 6\ e^- \tag{4}$$

Electrolytic experiments in a beaker, in which either a steel plate or a saturated sodium amalgam was used as the cathode, agreed fairly well with the theoretical gas composition considered above (Table 1).

Based on the above considerations and the experimental results, the abnormal electrode reactions would take place from around 3.38 p.m. in the cells when the sudden fall in the DC current was noticed. This would form an explosive gas mixture composed of hydrogen–chlorine mixture during early stages and hydrogen–oxygen mixture later. This would then be carried forward to the chlorine drying towers.

The likely ignition sources in the drying towers

(1) Heat of dilution of sulphuric acid with water would increase the temperature of itself by only 10 K in the first tower where the highest absorption rate of water can be expected. Data given in a reference show that the self-ignition temperature of H_2–Cl_2 mixture is about 94°C [2]. Thus the cause of the ignition cannot attributed to this effect.

(2) The effect of the adiabatic compression by the compressor could easily raise the temperature of gases to ~94°C. However, the main explosive gas mixture, H_2–O_2 in this case, has a self-ignition temperature > 500°C. Further, the explosion did not extend to the turboblower which was situated at the end of the tower chain. Therefore, this effect can also be discounted.
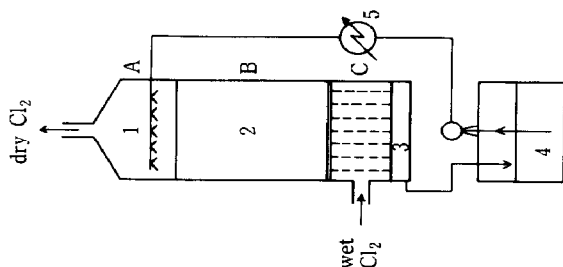
Fig. 7. A diagram of a chlorine drying tower. Key: 1, sulphuric acid distribution tray; 2, Raschig ring layer; 3 and 4, sulphuric acid sink; 5, cooler.

(3) In the H_2–Cl_2 system some chain reaction can occur to form hydrogen chloride by the ultraviolet irradiation below 400 nm. The inspection revealed that the towers were not fitted with sight glasses from where the rays of sun light could enter. Besides, it is known that the chain reaction of the H_2–Cl_2 system is interrupted by the presence of oxygen. Thus, there is little likelihood that this caused the explosion.

(4) To study any possible catalytic effect, some experiments were carried out. A result showed that HgO can react with Cl_2 to form Cl_2O, which can explode easily at near room temperature. This fact agrees with a previous report [3]. Results of an analysis of deposits attached to the Raschig rings or to the inside of the towers showed that the maximum concentration of Hg in the deposits was only 5 ppm. Thus, even if all the Hg atoms were in the form of HgO, they could not be the likely ignition source. No other substances were found which could have had any catalytic effect.

(5) As a result of the inspection, it was confirmed that there was no possibility of a spark from the mechanical tools used during the repair work on the second tower or from the electrical instruments installed on the towers to provide an ignition source. Resistance thermometers installed in the chlorine outlets of each tower and a sensor for the differential pressure gauge at the chlorine outlet of the last tower were undamaged. Besides, these had no structures producing any hot spot.

(6) Lastly, the possibility of an electrostatic discharge in the chlorine drying towers was considered.

Irrespective of whether mercury amalgam cells or diaphragm cells are used, chlorine gas must be first cooled and then dried before further processing. A diagram of a drying tower is given in Fig. 7. They are cylindrical vessels, 1–2 m in diameter, 8–10 m high and 15–20 mm in wall thickness, filled with a packing material such as Raschig rings. Concentrated sulphuric acid is pumped to the top of the tower and wet chlorine gas is sucked to the bottom of the tower by a suction fan installed at the end of the tower chain. Dehydration is carried
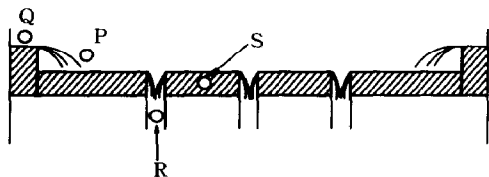
Fig. 8. Flow state of sulphuric acid at its distribution tray. O, position of the probe of an electro-static potentiometer; P, near the space where sulphuric acid flows down generating spray; Q, above the surface of sulphuric acid; R, in the pipe where sulphuric acid flows down continuously; S, in the liquid of sulphuric acid.

out by sulphuric acid flowing down the Raschig rings countercurrently with chlorine gas.

Case histories show that whenever an explosive gas mixture such as H_2-Cl_2 or H_2-O_2 happens to be carried forward to the drying tower, which is made of a non-conductive material such as PVC, an explosion infallibly occurs. There-fore, it has been suspected that the likeliest source of ignition in the towers would be the discharge sparks resulting from the electrostatic charge in the tower caused by sulphuric acid drops. This is likely to occur when sulphuric acid is in contact with any non-conductive material such as PVC to form an electrical double layer, which separates and becomes electrostatically charged. However, little research data are known at present whether the drying towers are actually electrostatically charged or not.

Measurement of electrostatically charging state of a chlorine drying tower

Measurement of the actually charging state of a chlorine drying tower, made of PVC, was carried out in the Tsurumi Soda Co., Ltd. near Yokohama on October 15, 1975 (Fig. 7).

(1) Electrostatic potentials of about plus 100 V were detected around the tower top A using an electrostatic radioisotope-type potentiometer. Compa-rable potentials were also detected on the side wall of the space below the Ras-chig ring layer C. But, no charge was detected on the side wall of the Raschig ring layer B. The pointer of the potentiometer showed such a behaviour on the dial plate that, as the probe approached the tower wall, it drifted gradually from zero position towards the positive side and then returned suddenly to zero, when the probe came at a certain distance away from the tower wall.

(2) Noises in the high frequency band, caused by the electrostatic discharge in the tower, were detected using an amplifier modulation radioset. More fre-quent noises were clearly heard at C than at A. No noises were heard at B.

(3) The sulphuric acid distribution tray is situated inside the point A and its section is shown in Fig. 8. In the vicinity of points such as P where sulphuric
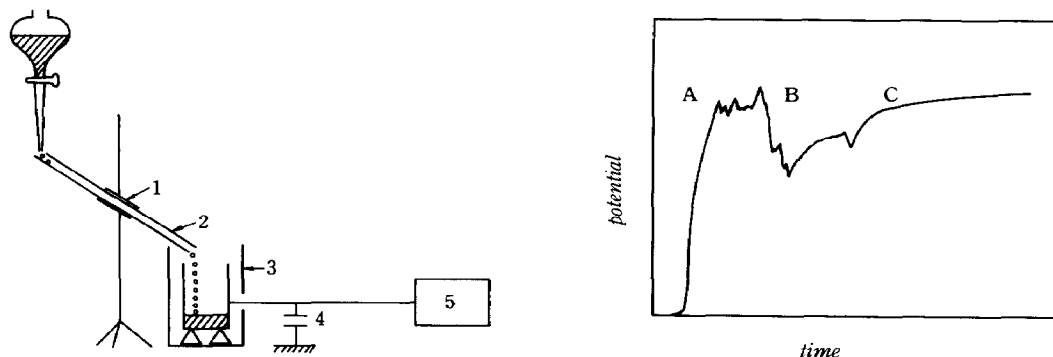
Fig. 9. An experimental set-up on electrostatically charging phenomena of sulphuric acid when flowing down from a PVC pipe. Mean weight per droplet was about 0.056 g. Key: 1, teflon sheet; 2, PVC pipe, 1 in. in diameter, 1 m long; 3, Faraday cage; 4, condenser, 490 pF; 5, electrometer and recorder.

Fig. 10. Electrostatically charging phenomena of sulphuric acid when flowing down continuously. Units of both axes are arbitrary.

acid flows down generating spray, charges of about plus 20 V were observed. No charge was detected at points such as Q, R or S.

(4) It was observed that a large portion of sulphuric acid flowed down below the Raschig ring layer as liquid columns, but at the same time the space was filled with a mist of sulphuric acid. Electrostatic potentials of about minus 5 kV were repeatedly detected whenever the probe of the potentiometer was inserted from the outside into a hole which was drilled in the side wall.

Experiments on electrostatically charging phenomena of sulphuric acid flowing down from a PVC pipe

Sulphuric acid (98%) becomes charged positively when dripping down from a PVC pipe, which is charged negatively (Fig. 9). The electrostatic charge per droplet showed a constant value of ca. 8×10^{-12} C, irrespective of the rate of dripping. This corresponds to a potential rise per droplet of 0.017 V with the above experimental set-up. It was also observed that the charged sulphuric acid droplets dispersed as mist just after having separated from the PVC pipe.

When sulphuric acid flows down continuously (Fig. 10), the electrostatically charging phenomena depend largely on its flow rate, and no stable charge accumulation occurs when flowing down continuously as a liquid column. In stage A, a clear rise in the potential can be seen during the early stages of the sulphuric acid flow, because it drips for a while as its flow rate gradually increases. In stage B, after the pipe and the receiver became connected by a liquid

column of sulphuric acid, the charge accumulation became unstable, as stated above. At the final stage of sulphuric acid flow (stage C) the rise in the potential is again observed as the dripping phenomenon reappears with the decrease of the flow rate.

Conclusions

It can be concluded from the above experiments that sulphuric acid becomes charged when it is dispersed as a mist or droplets, but does not when it is flowing as a continuous column. The possible ignition places in the towers where an explosion is likely are the spaces above and below the Raschig ring layer, where sulphuric acid mist or droplets will be present. Almost all case histories of similar accidents known hitherto confirm this conclusion.

A charge recombination in charged mist or droplets, in the tower, is not easy because the mist consists of separate particles insulated from one another. But, the total charge in a sulphuric acid mist may reach eventually such a level that an electrostatic discharge is possible to a prominent part in the tower body or to an earthed probe introduced into the tower.

The fundamental preventive measures for an electrostatically charging phenomena of the towers are, therefore, either to create situations such that sulphuric acid flows down continuously as a liquid film from the distribution tray down to the bottom of the tower over the surface of tower wall and packings, or to construct the towers of some acidproof and conductive material, so that the tower structure and sulphuric acid can be held at the earth potential. There is a tendency to use materials such as carbon fibre reinforced polypropylene resin, called CFRPP, for the latter purpose in Japan [4–7]. A typical composition and property of CFRPP is such that with the carbon fibre of 10 wt%; conductive carbon black, 10 wt%; the volume resistivity is $10^2 \sim 10^4 \ \Omega$cm. It was confirmed that the electrostatically charging phenomena was completely eliminated with a miniature set of the drying tower made of CFRPP [4].

Safety precautions

(1) Install a current breaker of sufficient capacity to deal with an abnormal load.

(2) The AC power supply for control, measuring and alarm system should be taken from separate sources other than that for the mercury pumps of the DC power supply. The control, measuring and alarm systems must be capable of operating during a plant failure. A emergency power supply for this purpose should be considered.

(3) The continuous hydrogen analysers should be installed on the chlorine outlets of each cell to enable it to monitor any change of hydrogen concentration within as short a time as possible.

(4) Install an interlock system between the DC power supply to the cells

and the AC power supply to the mercury pumps, and so also between the DC power supply and the continuous hydrogen analysers, so that an interruption of the power supply or an abnormal sudden increase of hydrogen concentration would shut down the entire plant.

(5) As for the shape of the towers, each chlorine gas outlet should be placed at the highest point of a tower, and not at its side wall. A conical, not a cylindrical, shape is desirable for the top part of the tower to eliminate any dead pockets where hydrogen gas could accumulate.

(6) An acidproof and conductive material should be adopted for the construction of the towers, so that the tower structure can be held at the earth potential, with sulphuric acid, to eliminate completely the electrostatically charging phenomena.

Acknowledgements

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