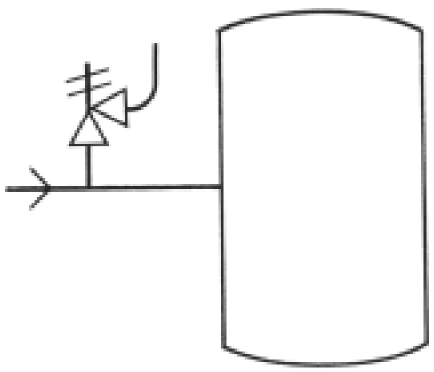
IMPERIAL CHEMICAL INDUSTRIES LIMITED
PETROCHEMICALS DIVISION

SAFETY NEWSLETTER No 70

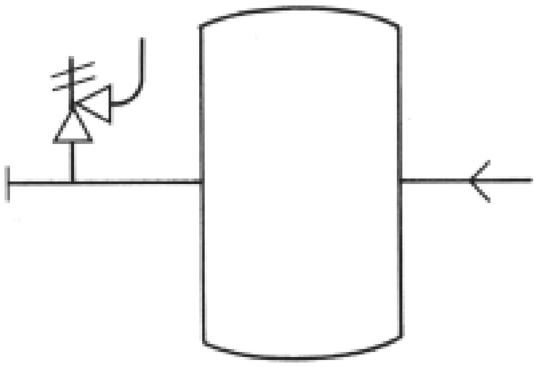
70/1 A RELIEF AND BLOWDOWN REVIEW OF A NEW PLANT - AFTER START UP

Last year the Division started up a new plant. As usual, a complete relief and blowdown review was carried out during design.

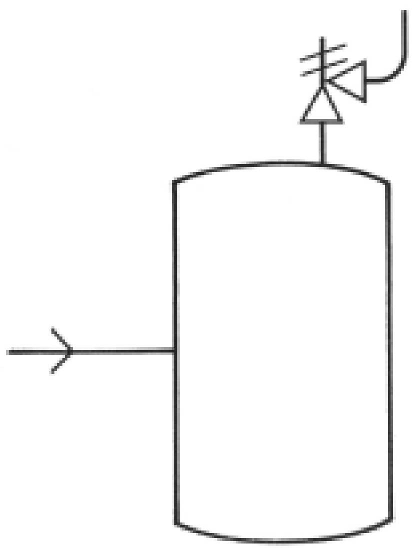
A year after start-up the relief and blowdown review was repeated. In twelve instances, the assumptions of the original review were found to be no longer true, and additional or larger relief valves, or changes in the position of a relief valve, were found to be necessary. The following are some examples.



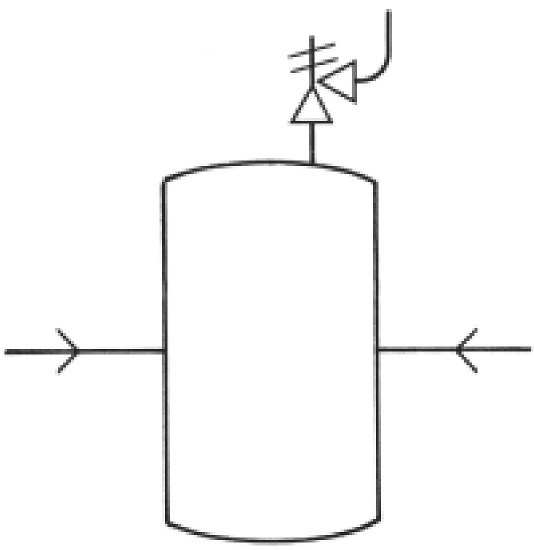
The relief valve was fitted on the inlet branch so that the flow would keep the branch clear.



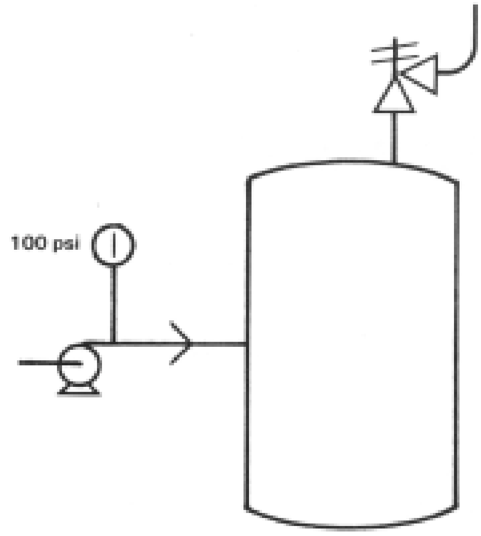
The inlet was moved to a new position leaving the relief valve on a ‘dead-leg’.



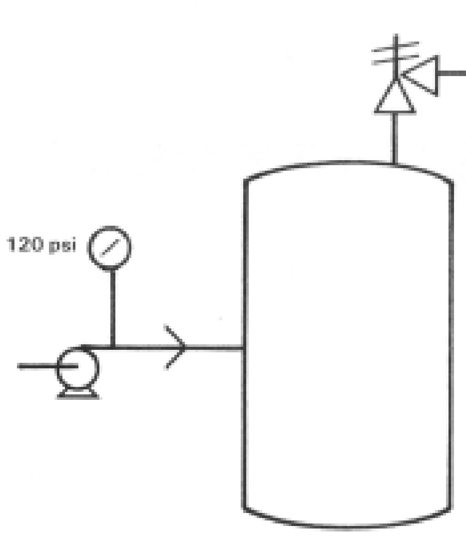
The relief valve was sized to take the full inlet flow with all exit lines closed.



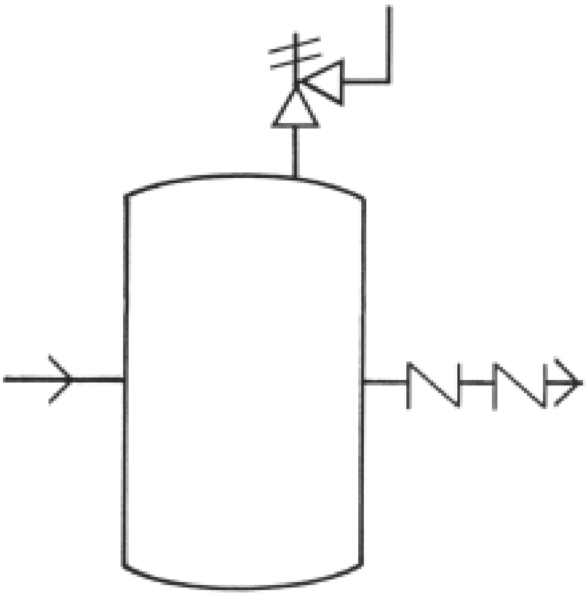
An extra inlet line was added. If both lines are used together the relief valve will be too small.



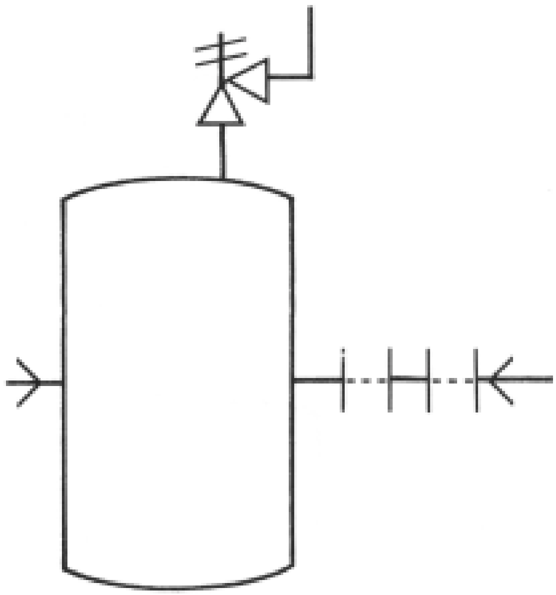
The vessel was designed to withstand the maximum pressure the pump could deliver. The relief valve was not designed to take the maximum flow from the pump.



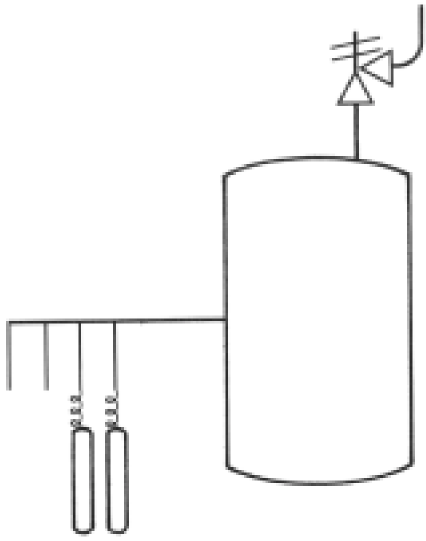
The pump actually proved capable of producing 20 psi more than design. If the exit from the vessel is isolated when the pump is running the vessel will be overpressured



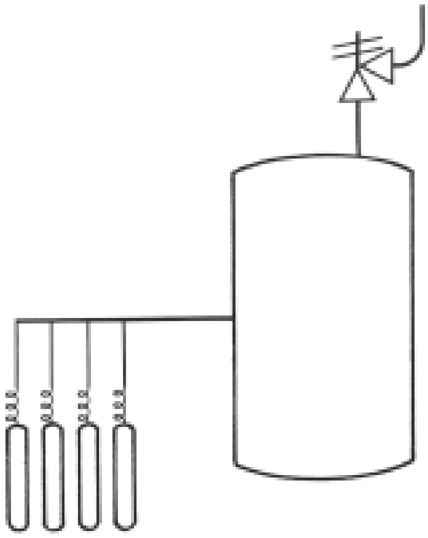
The relief valve was sized on the assumption that two non-return valves in series would prevent back-flow into the vessel.



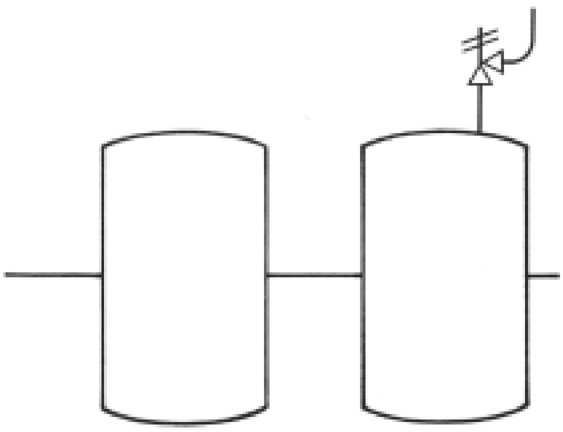
Both non-return valves corroded, allowing back-flow to take place.



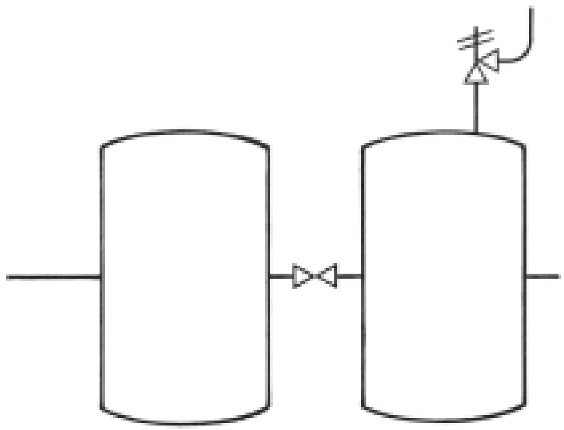
The relief valve was sized on the assumption that only two gas cylinders would be used at a time, though connections were provided for four cylinders.



Inevitably, four cylinders were connected up and some-times used.



A single relief valve was designed to protect two vessels which were connected together by a line without any valve or other restriction between them.



An extra isolation valve was fitted between the two vessels, thus making it possible to isolate the first vessel from its relief valve

In another similar case, chokes occurred in the line between the two vessels.

The line diagrams had been kept up-to-date despite the pressures on the plant staff during start-up and this made it easier to repeat the relief and blowdown review. The plant staff were so impressed by the results that they have decided to have another look at the relief and blowdown after another year.

Have you checked the relief and blow-down review on your plant since start-up?

Have you got procedures for making sure that modifications are checked *at the time* for these affects on safety.

70/2 "EMERGENCY ISOLATION OF CHEMICAL PLANT"

Earlier Newsletters (62/2, 60/1, 51/3, 41/12a, 39/2, 27/3, 14/1) have described many leaks and fires which were, or could have been, controlled by the use of remotely-operated emergency isolation valves.

The ICI Process Safety Panel have now issued a Guide on the "Emergency Isolation of Chemical Plant". It is intended to help plant operators and designers decide when remotely operated emergency isolation valves should be installed and to help them choose suitable types.

A number of incidents which could have been prevented by the use of emergency isolation valves are described and some typical installations are described in detail.

Copies of the Guide can be obtained from Division Reports Centres by asking for Report No.

HO/S D/74001 0/1.

70/3 WHAT IS A FLASHING LIQUID AND WHY IS IT SO DANGEROUS?

Several readers have asked me to explain why a leak of a flashing liquid is more dangerous than a leak of a gas or a leak of an ordinary liquid.

Suppose a plant contains a flammable liquid such as petrol at atmospheric temperature and 100 psig; suppose a 2 inch diameter hole appears in the plant in the open air — it might be caused by corrosion or someone may leave a drain valve open or leave off a blank. Petrol will come out at a rate of about 180 tons/hr. It will form a pool of liquid on the ground, but the vapour will extend only about 10 feet downwind and about 2 feet upwards. Even if the leak goes on for a very long time and a very large pool is formed, the vapour is unlikely to extend further away than a distance equal to the diameter of the pool. If the vapour catches fire there will be a big fire but an explosion is very unlikely

Of course, if the leak is inside a closed building, the whole building can fill with vapour and an explosion is possible. This is why we like to have all our equipment in the open air.

Now suppose a 2 inch diameter hole appears in a plant handling a flammable gas such as propylene at atmospheric temperature and 100 psig. The quantity of material which comes out is much less, only about 15 tons/hr, but it is all vapour. If the vapour has a clear, uninterrupted escape path it will be diluted with air by jet mixing to a safe level. A serious explosion is impossible, but, if the vapour ignites, there could be a pop and there will be a nasty fire, like a torch, close to the leak. If the vapour impinges on the ground or another pipe it will not be diluted so quickly, a cloud will form and an explosion is possible.

Consider now a plant containing petrol at 120°C and 100 psig. The petrol is above its normal boiling point, which is about 100 °C. The petrol will leak out of the pipe at about the same rate as in the first example, but the moment it comes out about one-eighth of it will evaporate or "flash", and much of the rest will be carried into the air as a fine spray, which is almost as dangerous as the vapour. A large cloud of vapour and spray will be formed, much bigger than in the first case.

Liquid propylene at atmospheric temperature behaves similarly. Its normal boiling point is -47°C and as it comes out of the hole, one-third of it will evaporate or "flash" and most of the rest will form a spray. It will come out at a rate of about 50 tons/hr, and in a 5 mph wind the vapour cloud will extend for about 370 ft.

If the holes are larger, leak rates will be greater. A 4 inch diameter hole will produce leak rates four times as great as those quoted above, and the vapour clouds will extend further. Even when these very big clouds ignite there is, as explained in Newsletter 60/6, usually only a pop followed by a serious fire close to the leak. Occasionally, however, if the vapour cloud is large and is mixed with air to just the right proportion, there can be a very big bang which produces a pressure of about 10 psig, sufficient to push over most buildings and plant structures.

A large, well-mixed cloud can be formed in two ways. First it can be formed by the jet action of the escaping vapour. The speed of the jet must be just right. If it is too fast the vapour will be diluted to a safe level; if the speed of the jet is too low the cloud will not contain enough air.

Second, it may be possible for a large, well-mixed cloud to be formed by the action of the wind. The leak must go on for a long time and the wind speed must be just right — not so strong that the vapour is blown away, and not so gentle that it does not mix in enough air.

I said before that to get a big bang the vapour cloud must be large. Five tons has been suggested as the minimum size, but one plant has been destroyed by the explosion of a vapour cloud which contained only ¼ ton.

So we see why leaks of a flashing liquid are much more dangerous than leaks of ordinary liquids or leaks of gas.

So far I have talked about flammable gases and liquids, but the same arguments apply to toxic ones. Ammonia is sometimes handled as a gas, sometimes as a refrigerated liquid at atmospheric pressure and -33°C, and sometimes as a flashing liquid under pressure at ordinary temperature. A leak of gas is not the most dangerous as not so much comes out. A leak of a refrigerated liquid is not the most dangerous as it evaporates slowly, but a leak of ammonia under pressure at atmospheric temperature is much more serious; 15% of the liquid evaporates and the rest is carried into the atmosphere as spray, which evaporates as it picks up heat from the surroundings.

70/4 ANOTHER SERIOUS INDUSTRIALACCIDENT WITH LESSONS FOR US ALL

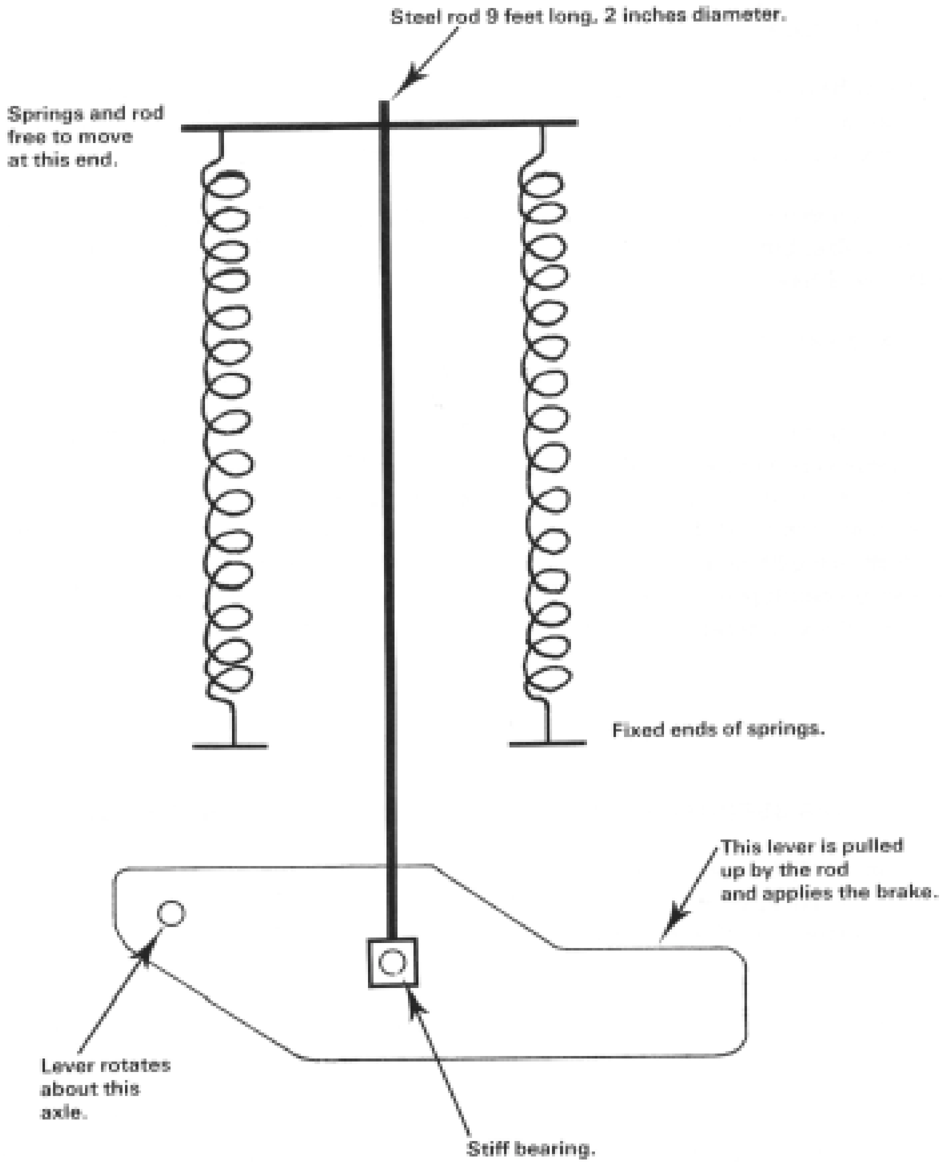
The explosion at Flixborough was not the only serious industrial accident that has occurred in recent years. The collapse of a cage at Markham Colliery, Derbyshire in July 1973 killed 18 men and seriously injured 11. The official report tells a story that will interest everyone concerned with industrial safety.

The accident could have been prevented — like so many others — by better design or by better management and — in particular — by taking note of the lessons of the past.

Let us start by looking at the design — the hardware as it is often called. When the accident occurred the newspapers said that about sixteen separate safety systems had to fail before the cage could collapse.

However the report shows that all these safety systems operate the same brake — and the brake failed. (It is rather like some of our plants in which a high temperature trip, a high pressure trip, a high level trip and a push-button all close the same motor-valve. The motor-valve is ‘single-line’ and if it fails, all the trips fail.)

The brake is applied by powerful springs, held off by compressed air. The springs act through a steel rod, 9 feet long and 2 inches in diameter, which operates a lever.



The bearing at the bottom of the rod could not be oiled. It got stiff, the rod got bent and as a result the stress on it was excessive. It broke.

Now let us look at the management system - the software as it is often called.

A similar brake failed in the same way in 1961, though without serious consequences. The design was not changed but the Divisional Chief Engineer issued an instruction that all similar rods should be examined He did not say how they should be examined or how often. At Markham Colliery the brake rod was examined in position but was not removed for complete examination and was not scheduled for regular examination in the future.

The winding engine and brake were tested every three months but the loads used were only estimated and were sometimes less than the normal working load.

The official report ("Accident at Markham Colliery, Derbyshire") can be obtained from the Stationery Office, price £1.10.

Finally, I would like to quote from another official report, that on the collapse of a colliery tip at Aberfan in October 1966, in which 144 people, 116 of them children were killed.

"The - - - disaster is a terrifying tale of - - - failure to heed clear warnings - - - . Not villains, but decent men, led astray by foolishness or ignorance or both in combination, are responsible for what happened".

70/5 SOME QUESTIONS I AM OFTEN ASKED

5 - MEN ARE UNRELIABLE SO SHOULD WE TRY TO MAKE OUR PLANTS FULLY AUTOMATIC?

It is true that men are never as reliable as we would like them to be — see for example Safety Newsletter No 66/3. However, when we make a plant fully automatic *we do not remove our dependence on human reliability, we merely transfer it from one man to another.*

Suppose there is a red light in the control room and when it comes on the operator has to go outside and close a valve. The red light might indicate a high level in a tank and the valve might be on the inlet line to the tank. Sooner or later the operator will fail to close the valve, the tank will overfill and somebody will suggest that the high level ought to close the valve automatically.

If we do this then we have removed our dependence on the operator but we are now dependent on the instrument artificer and electrician maintaining the trip and alarm light correctly and checking it regularly. We are still dependent on human reliability.

Of course, in a case like this, it is often right to replace an operator by a trip. The process operator may be under stress or very busy while an instrument artificer tests and maintains the trip under conditions of less stress, but we must not kid ourselves that we are no longer dependent on men; we are merely dependent on different men.

70/6 UNUSUAL ACCIDENTS NO 40 - AN EXPLOSION IN A CARGO OF BANANAS

A ship carrying a cargo of bananas caught fire, and during the fire-fighting an explosion occurred injuring seven firemen and two other people.

The Annual Report of H M Inspectors of Explosives for 1973 reports this incident (on page 13) and suggests that, as a small amount of ethylene is used to ripen bananas, the heat from the fire caused the bananas to give off ethylene, which then formed an explosive mixture.

It is more likely that the heat caused the bananas to give off oil which, at the temperature reached, formed an explosive mixture with air. Banana skins are quite oily. It is said that if your gearbox runs out of oil, you can stuff it with banana skins.

(Reminder: For other examples of heavy oils exploding when hot, see Newsletters 5 1/2, 24/6, 18/7e)

70/7 RECENT PUBLICATIONS

(a) As reported in Newsletter 58/9c, ICI is collaborating with other chemical companies to produce a series of Codes of Practice on the storage and handling of hazardous chemicals. The following are now available and can be obtained from Division Reports Centres.

	Ref No
No 1 Chlorine	HO/SD/73006/1
No 2 Hydrogen Fluoride (Anhydrous)	/2
No 3 Phosgene	/3
No 4 Hydrogen Chloride (Anhydrous)	/4
No 5 Ethylene Dichloride	/5

(b) Fire Research Note No 1003, available from the Fire Research Station, Borehamwood, Herts, WD6 2BL, shows that steel solvent cupboards give less protection than wooden cupboards. Our own tests confirm this; intumescent paint gives added protection. (Reminder: Newsletter 67/7b reported that if bottles can be exposed to fire, plastic caps are better than metal ones, as the plastic melts, relieves the pressure and prevents the bottle bursting).

(c) "Incidents in the Oil Industry" No 12 describes a number of fires and spillages which have occurred during the storage and handling of hydrocarbons.

(d) Safety Note 74/13 describes the uses and limitations of steam curtains. It shows how to decide whether or not to install one and outlines the method of design.

(e) We have a few of our 1975 Safety Calendars to spare. They will be given to the first people who apply.

For copies of (c) — (e) or for more information on any item on this Newsletter, please write to E.T. or phone ext. P.2845. If you do not see this Newsletter regularly and would like your own copy, please ask Mrs T. to add your name to the circulation list.

Best wishes to all our readers for a Merry Christmas and a safe New Year.

November 1974

SUPPLEMENT ON THE FEASIBILITY OF COAL-DRIVEN POWER STATIONS

It is easy to exaggerate the dangers of new inventions, like atomic power stations, and to forget about the familiar dangers of mining and coal burning. The following article by 0 A Frisch, written in 1955, assumes that atomic power stations have been in use for thousands of years, and that coal burning has just been re-invented.

The following article is reprinted from the Yearbook of the Royal Institute for the Utilization of Energy Sources for the Year 4955.

In view of the acute crisis caused by the threat of exhaustion of uranium and thorium from the Earth and Moon Mining System, the Editors thought it advisable to give the new information contained in the article the widest possible distribution.

Introduction. The recent discovery of coal (black fossilized plant remains) in a number of places offers an interesting alternative to the production of power from fission. Some of the places where coal has been found show indeed signs of previous exploitation by prehistoric men who, however, probably used it for jewels and to blacken their faces at tribal ceremonies.

The power potentialities depend on the fact that coal can be readily oxidized, with the production of a high temperature and an energy of about 0.0000001 megawattday per gram. This is, of course, very little, but large amounts of coal (perhaps millions of tons) appear to be available.

The chief advantage is that the critical amount is very much smaller for coal than for any fissile material. Fission plants become, as is well known, uneconomical below 50 megawatts, and a coal-driven plant may be competitive for isolated communities with small power requirements.

Design of a coal reactor. The main problem is to achieve free, yet controlled, access of oxygen to the fuel elements. The kinetics of the coal-oxygen reaction are much more complicated than fission kinetics, and not yet completely understood. A differential equation which approximates the behaviour of the reaction has been set up, but its solution is possible only in the simplest cases.

It is therefore proposed to make the reaction vessel in the form of a cylinder, with perforated walls to allow the combustion gases to escape. A concentric inner cylinder, also perforated, serves to introduce the oxygen, while the fuel elements are placed between the two cylinders. The necessary presence of end plates poses a difficult but not insoluble mathematical problem.

Fuel elements. It is likely that these will be easier to manufacture than in the case of fission reactors. Canning is unnecessary and indeed undesirable since it would make it impossible for the oxygen to gain access to the fuel. Various lattices have been calculated, and it appears that the simplest of all — a close packing of equal spheres — is likely to be satisfactory. Computations are in progress to determine the optimum size of the spheres and the required tolerances. Coal is soft and easy to machine; so the manufacture of the spheres should present no major problem.

Oxidant. Pure oxygen is of course ideal but costly; it is therefore proposed to use air in the first place. However it must be remembered that air contains 78 per cent of nitrogen. If even a fraction of that combined with the carbon of the coal to form the highly toxic gas cyanogens this would constitute a grave health hazard (see below).

Operation and Control. To start the reaction one requires a fairly high temperature of about 988°F; this is most conveniently achieved by passing an electric current between the inner and outer cylinder (the end plates being made of insulating ceramic). A current of several thousand amps is needed, at some 30 volts, and the required large storage battery will add substantially to the cost of the installation.

There is the possibility of starting the reaction by some auxiliary self-starting reaction, such as that between phosphine and hydrogen peroxide; this is being looked into.

Once the reaction is started its rate can be controlled by adjusting the rate at which oxygen is admitted; this is almost as simple as the use of control rods in a conventional fission reactor.

Corrosion. The walls of the reactor must withstand a temperature of well over a 1000°F in the presence of oxygen, nitrogen, carbon monoxide and dioxide, as well as small amounts of sulphur dioxide and other impurities, some still unknown. Few metals or ceramics can resist such gruelling conditions. Niobium with a thin lining of nickel might be an attractive possibility, but probably solid nickel will have to be used. For the ceramic, fused thoria appears to be the best bet.

Health Hazards. The main health hazard is attached to the gaseous waste products. They contain not only carbon monoxide and sulphur dioxide (both highly toxic) but also a number of carcinogenic compounds such as phenanthrene and others. To discharge those into the air is impossible; it would cause the tolerance level to be exceeded for several miles around the reactor.

It is therefore necessary to collect the gaseous waste in suitable containers, pending chemical detoxification. Alternatively the waste might be mixed with hydrogen and filled into large balloons which are subsequently released.

The solid waste products will have to be removed at frequent intervals (perhaps as often as daily!), but the health hazards involved in that operation can easily be minimized by the use of conventional remote-handling equipment. The waste could then be taken out to sea and dumped.

There is a possibility — though it may seem remote — that the oxygen supply may get out of control; this would lead to melting of the entire reactor and the liberation of vast amounts of toxic gases. Here is a grave argument against the use of coal and in favour of fission reactors which have proved their complete safety over a period of several thousand years. It will probably take decades before a control system of sufficient reliability can be evolved to allay the fears of those to whom the safety of our people is entrusted.