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Technical Bulletin

SULPHIDATION

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BACKGROUND:

A large proportion of natural gas comes from gas-fields in the North Sea through the two inter-connectors. Unlike the gas from the Kinsale fields this gas contains a trace of Hydrogen Sulphide (H_2S) which may react with the copper pipe and copper components in appliances. The hydrogen sulphide causes a black deposit to form on the inner walls of the copper pipe - Copper Sulphide (Cu_2S). This is called 'Sulphidation'. In some circumstances this deposit is in form of flakes. These flakes can become detached and get carried by the gas flow into appliances, where they can accumulate and restrict the flow of gas through apertures in injectors, and through valves, filters, pilot lights, etc., causing loss of output, and eventually the failure of the appliance to function.

Sulphidation can occur when the Hydrogen Sulphide content is above 0.4 mg/m^3 , but until the levels are more than about $1.5 - 2.0 \text{ mg/m}^3$ it does not seem to cause many problems. The gas landed at the St Fergus terminal in Scotland, for example, had a hydrogen sulphide content of only 0.6 mg/m^3 when it first came on stream in 1986, but this was found to increase particularly in the 90's, and is now at 3.5 mg/m^3 . In view of this the number of instances of sulphidation in Ireland may increase in the years ahead.

In rare instances, the effects of sulphidation become immediately apparent but typically it takes about three or more years before problems arise. The copper has to react with the Hydrogen Sulphide to form a deposit which might in due course flake off. The gas flow must be fast enough to cause these flakes to travel with the gas to a collection point, where they may then accumulate and interfere with appliance operation.

Not all copper pipe will react with the hydrogen sulphide in the gas to form the troublesome flakes, and the reasons for this are not yet clear. Based on the experience in the UK (where the sulphidation problem has occurred in Scotland and in the North of England and Wales), it is likely that less than 0.5% of the domestic sized installations might be effected. In Ireland, this would indicate that between 2,000 and 2,300 installations might be affected to varying degrees.

The copper sulphide deposits have the appearance of small graphite flakes and are sometimes referred to as 'Black Dust'

OCCURRENCE AND EFFECTS OF SULPHIDATION:

Of the following known factors which may influence the occurrence of sulphidation in copper, only the first four can be modified in practice to minimize or eliminate the problem, and this only in new installations -

- (a) the output of the appliance and the rate of flow of gas through the pipe
- (b) the choice of pipe material
- (c) the orientation and size of the pipe
- (d) the rate of Cu_2S production which effects subsequent deposit stability
- (e) the H_2S content of the gas
- (f) the size of the injectors or burner units
- (g) the presence of traces of oxygen and of water in the gas
- (h) the temperature of the copper in contact with the gas

The effects of the copper sulphide detaching from the copper surface and being transported in the natural gas to the gas appliance are as follows;

- (a) Collection of deposits in multi-port injectors, particularly in gas fires, possibly leading to poor combustion.
- (b) Deposits within gas valves leading to boiler or other appliance malfunction.
- (c) The pilot light (flame) losing shape, causing cooling of the thermocouple and appliance shut down.
- (d) Small amounts of gas let-by is also possible where deposits affect a valve seating.

Undergassing of appliances can occur where on-line filters have been fitted and are not serviced sufficiently regularly. Undergassing of appliances results in inefficient combustion and instability of the flame.

Fires and back boiler are particularly susceptible.

For gas consumers with frequently affected appliances this can be a major nuisance.

REMEDIAL ACTION

New Installations

Copper pipe is a common choice for domestic sized installations, however other materials such as *corrugated stainless steel tubing* may be used as an alternative and thus avoid the risk of sulphidation occurring on the installation pipework.

Existing Installations

The following remedial actions are recommended;

1. Fitting of Filters

Filters can be fitted immediately before each appliance, a valve being fitted before each filter to allow for safe servicing. Filters will not prevent sulphidation occurring, but they will prevent the flakes being carried in to the appliance. Care must be taken in filter sizing to ensure this will allow them to collect the quantity of copper sulphide formed between service intervals, without causing undue pressure drop.

If filters are not serviced at appropriate intervals the build up of copper sulphide retained will increase the resistance to the flow of gas to the appliance. This may cause the gas pressure under full load conditions to become too low for satisfactory combustion and cause under-gassing. Each filter should have a pressure connection fitted immediately after it to allow the pressure to be verified under full load before servicing. This should be determined immediately after commissioning, and the pressures recorded and given to the Client. If on subsequent occasions the accumulation of deposits is found to cause too great a pressure drop the frequency of service must be increased.

It is important to clean the filters as part of the appliance service. Filters are not recommended for appliances without a flame failure safety device.

2. Blow through with Air

The open-ended carcassing can be blown through with air to remove any existing deposits in the pipework. This will extend the time between remedial actions.

3. Non copper appliance components

Where the problem occurs as a result of copper components in an appliance, the manufacturer can be contacted to check if a non-copper alternative is available.

4. Protective Internal Coating of Copper Pipe-work

A procedure to coat installed copper pipe-work internally where appliances are already installed has been developed in the UK. This patented process is known as 'Dust Stop'. The appliances are disconnected and all foreign matter is removed from inside the pipe by blowing through each branch separately with all others capped. The internal coating is then fed into a compressed air stream and adheres to the pipe, each branch being coated separately. Caps are then removed, and the entire assembly left open for about 60 minutes to allow the coating to set.

The pipe-work is then reconnected, the system tested for soundness, and operated briefly at maximum load whilst gas pressure at each appliance is measured to ensure it is satisfactory, and then recorded. The treatment is effective and has been used successfully in the UK for about ten years.

Since the treatment is labour intensive, it is expensive to apply to an installation.

A request to have an installation treated in this way can be made to, Technical Division, Bord Gáis Distribution, Donmoy House, St. Margaret's Road, Finglas, Dublin 11.

SAFETY IMPLICATIONS

The safety implications are not considered to be significant, however sulphidation may aggravate a second fault such as inadequate flueing or ventilation and may result in the release of combustion products containing higher levels of Carbon Monoxide.

Uniform corrosion arising from sulphidation of the copper carcassing does not result in a significant risk of pipe failure. (The rate of corrosion by H₂S and removal of copper is extremely low.)

Let-by of gas as a consequence of sulphidation has been extensively studied by the UK Health and Safety Executive. It has been established that the quantities of gas, which may be let-by because of copper sulphide deposits affecting a valve, do not produce any significant safety risk.

To date there have been no reportable natural gas incidents in Ireland which are attributable to Sulphidation.

In the UK the Health and Safety Executive (HSE) have stated that there have been no reports of fatal or non-fatal incidents which can be attributed to sulphidation.

Other minor effects of the presence of traces of hydrogen sulphide in the gas can include; the corrosion of glass fronted fires, (principally an aesthetic problem) and a small increase of acid flue components, which again are unlikely to give rise to any safety issue.

As with all appliances, it is important to stress to the customer / owner of the premises the need for proper and regular servicing of appliances.