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Safety study concerning a phenolic resin injection procedure for ground reinforcement

Abstract

Polymer resins are used for ground reinforcement in coal mines. This is made necessary by the fracturing of the rock caused by the great depth of the mines, and the consequent problems of roof support.

In France, following a number of incidents resulting from the use of polyurethane resins, these materials have been replaced by phenolic resins for ground reinforcement.

INERIS has carried out a study of the process used in the mines for injecting phenolic resins. From the preliminary risk analysis conducted by INERIS on the entire process of injecting these phenolic resins - from the arrival of the reagents at the pithead through to their use underground - it appears that the risks involved in using phenolic resins are concentrated essentially in the polymerisation phase.

It appears from laboratory tests that the increase in temperature that accompanies the polymerisation of phenolic resins is appreciably less than that observed when polyurethane resins are used in comparable conditions.

Tests were carried out on greater quantities in order to characterise the risk that coal in contact with the phenolic resins during polymerisation would self-ignite. No coal ignition was observed in any of the tests carried out.

INTRODUCTION

The phenolic resins used in the ground consolidation process are produced *in situ* by mixing a preparation of resol and an aqueous solution of strong acid into an aqueous solution.

Resols are reactive phenolic resins involving methyl alcohol groups (- CH_2OH) or etheroxy links (-CH_2OCH_2-). These are produced by fixing formaldehyde on the phenol in an alkaline medium, producing a mixture of alcoholic phenols which react together as shown in figure 1 hereunder:

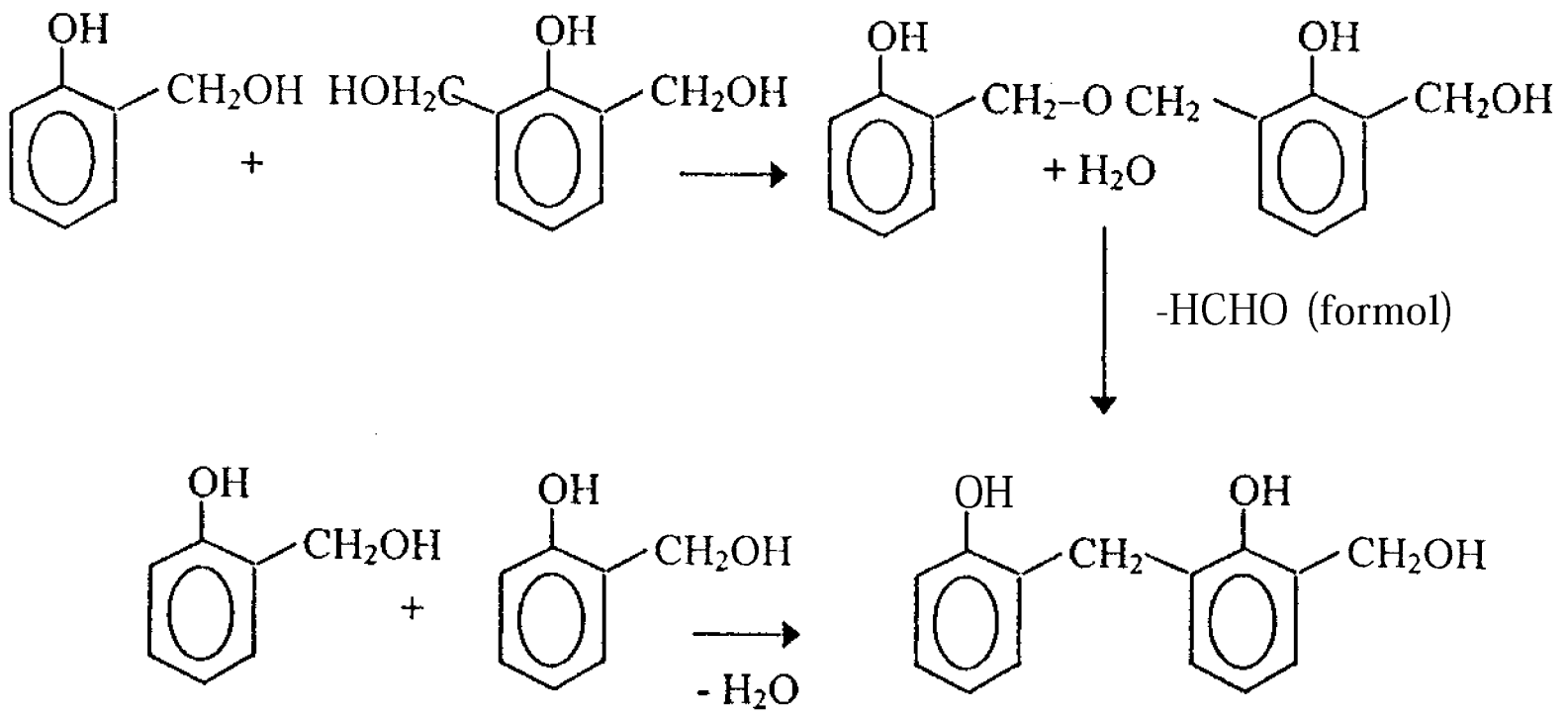

Figure 1. Reaction mechanism of phenol-formaldehyde polycondensation

The polycondensation occuring mechanism shown in figure 1 produces a three-dimensional lattice of the type shown in figure 2 :

This lattice structure can be held at a given degree of polymerisation by lowering the temperature.

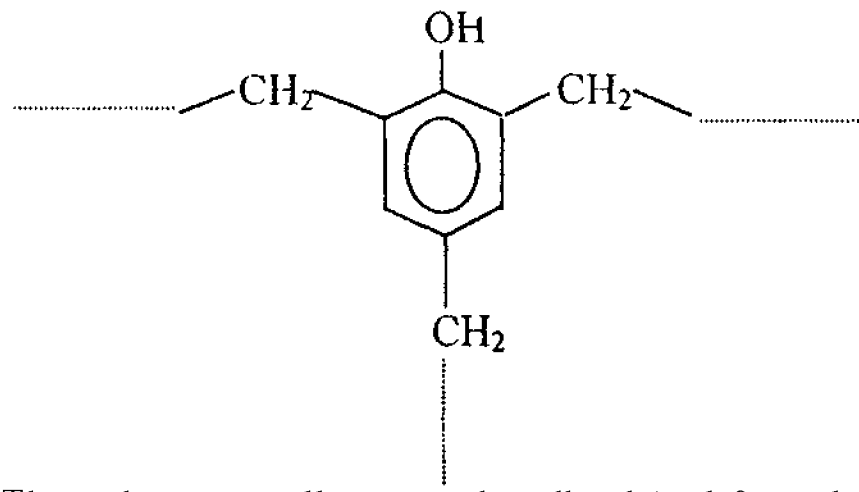

Figure2.Three-dimensionallatticeproducedbyphénol-formolpolycondensation

The resols used for ground consolidation are reactive liquid resins, of low molecular weight, the polymer lattice of which is of the type shown in figure 2. Adding an acid to a resol at room temperature causes the latter to harden by a curing mechanism of the type shown in figure 1 above. This structural process, which is accompanied by the release of heat, produces a mass of resin of high molecular weight.

It should be noted at once that the kinetics of the reaction between an acid and a resol and the degree of heat release depend on a number of parameters, including :

- the acid used and its concentration,
- the extent of polymerisation of the resols,
- the number and position of the reactive groups on the resols (- CH_2OH),
- the respective concentrations of formaldehyde and free phenol in the resols used.

The phenolic resins used for ground reinforcement are usually obtained by mixing two components - resin (based on resols in an aqueous solution) and catalyst (acid solution) in a volume ratio of 1 to 1.

The reagents (resin and catalyst) arrive on site and are stored at the pithead; they are then taken into the mines and stored near to the point of use, and finally injected into the ground requiring reinforcement.

The two components used for producing the consolidation resin (resin and catalyst) are pumped separately to the injection site where they are mixed and injected into cracks in the ground requiring consolidation.

This system is designed so that the two reagents (resin and catalyst) can be pumped simultaneously in a volume ratio of 1 to 1, the principle being shown in figure 3 hereafter.

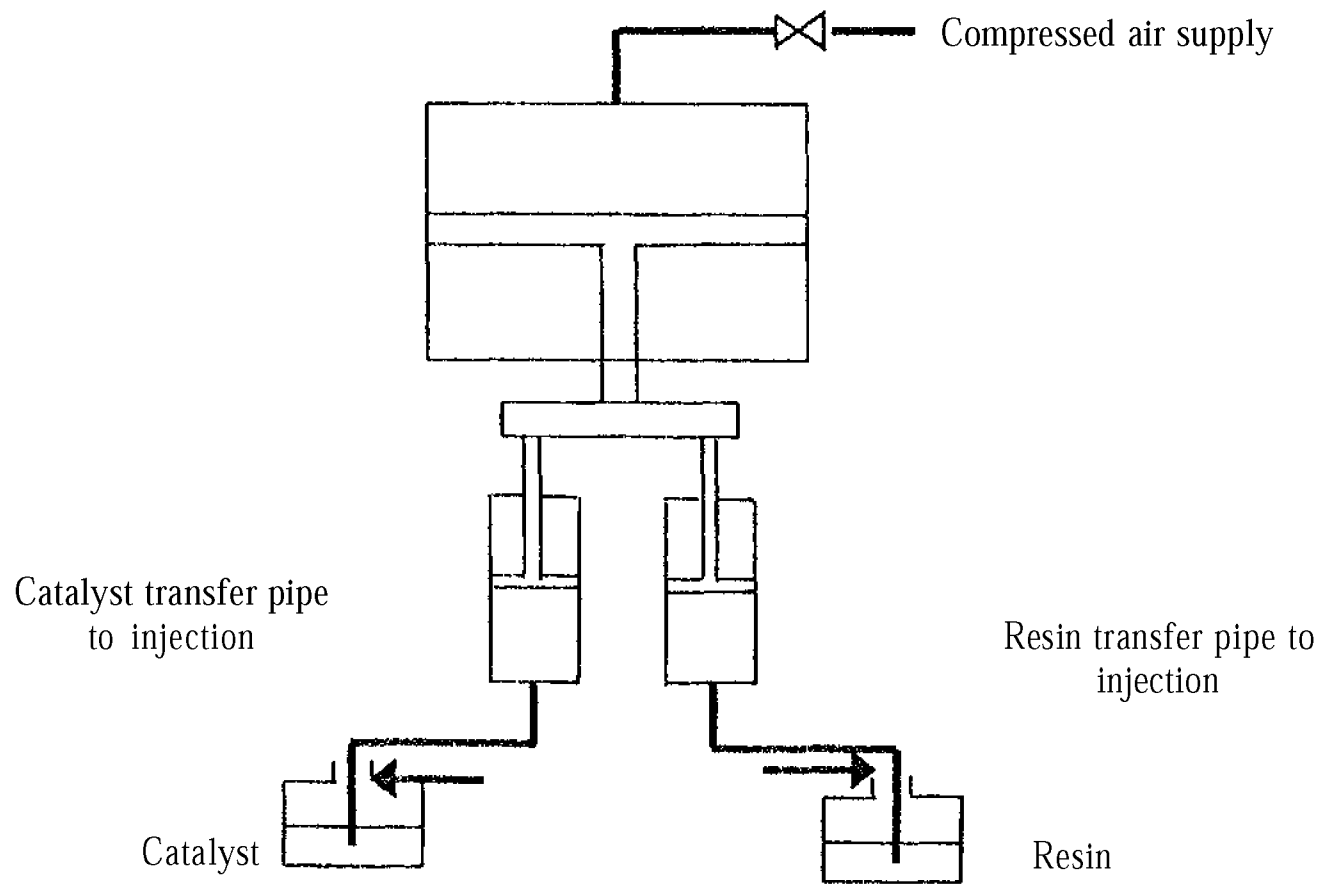

Figure 3. Operating principle of an injection pump

The two reagents (resin and catalyst) are pumped to the injection site through hoses inserted directly into their respective original containers. The two reagents pumped each through its own line as indicated above are then mixed actually at the injection point by means of a mixing gun in a three-branch Y configuration. Resin and catalyst are fed through the two upper branches of the Y into a static mixer.

EVALUATION

Methodology for hazard analysis

The aim of this hazard analysis is to identify any dangerous situations involved in using the equipment and products in the phenolic resin injection system.

The hazard analysis is concerned first with the hazards arising inside the injection process, related to the substances used and the equipment and, secondly, to those of external origin related to activities outside the process.

From a list of the different substances and systems present in the installations concerned by the study the relevant potential hazards are identified.

The hazard analysis is an analytical tool the aim of which is systematically to review facilities within which the process under investigation is applied. This method is applied by a working group in the framework of technical meetings.

The outcome of the group's considerations are set out in summary tables of the type shown in figure 4 hereunder.

No	Product or system	Hazardous situation	Causes	Consequences	Existing safety devices	Remarks	Proposals for improvements

Figure 4. Typical hazard analysis table used for safety studies relating to the process of injecting phenolic resins

The products and systems identified in the phase of describing the installations were reviewed, and the potentially hazardous situations (fire, explosion, leakage, corrosion, contamination, ...) examined.

For each combination of product/system and hazardous situation, the causes leading to the hazardous situation were sought and the impact on the installation and its environment determined.

The review of existing safety devices serves as a check on whether the hazardous situations revealed by the hazard analysis have been foreseen and are detected and, if appropriate, whether protective measures are planned to limit the consequences of potential accidents.

The operating status of each system is also taken into account: this may be normal operation, commissioning, shutdown, infrequent operating conditions (for example, system flushing) or transient. The search for the consequences of the situation under investigation can make use of the knowledge of incidents already noted.

On the basis of the hazardous situations revealed and having regard to the existing safety systems, INERIS is required to give an opinion on the preventive and protective measures liable to improve the safety of the phenolic resin injection process.

Application of the hazard analysis method to the process of phenolic resin injection

In view of the above description, the products liable to be used in the installations covered by the present safety study are:

- the component based on resol (resin),
- the acid catalyst (catalyst),
- the compressed air supply to the injection pump,

- the products used for flushing the pumping and injection lines.

The main areas and systems in which the phenolic resin injection process is utilised are:
- the reagent (resin and catalyst) reception area,
- the area at the pithead where the above reagents are stored,
- the route these reagents follow to reach the mine,
- the zone in the mine where the reagents are stored,
- the pumping system,
- the pipes carrying products to the injection site,
- the system for injecting resin into the rock,
- the rock into which the resin is injected.

The method already described was applied to each of the areas and installations listed above.

ANALYSIS

The hazard analysis carried out led to the identification of tests for characterising the inherent hazards in using the procedure for phenolic resin injection.

Toxicity

The liquid phenolic resins on the market are usually classified as non-toxic, so long as their free phenol content is limited [1]. Because the process of injecting phenolic resins necessitates a number of handling operations that could lead to one of the reagents used being released, the operator made sure, by means of tests carried out before application, that the chronic exposure limits were observed at all the workstations, notably below ventilation systems where personnel were likely to be present. Checks of this kind must be carried out at intervals, their frequency being determined by the operator's medical services.

As an illustration, the limiting exposure value for formaldehyde is 1 ppm, while the mean exposure value of this product is 0.5 ppm [2]. As regards phenol vapours, the mean exposure value is set at 5 ppm [2].

Thermal stability

As regards the resins used, Differential Thermal Analysis (DTA) tests were carried out by 1NERIS. These tests showed that the decomposition reaction of the resols becomes significant at about 250°C.

Similar tests revealed that the decomposition reaction of the catalyst becomes significant at about 350°C.

Finally, tests indicated that the thermal decomposition reaction of polymerised phenolic resins becomes significant at a temperature of about 270°C.

Reactivity

Reactivity tests were carried out on a number of mixtures containing, first, the basic components of the phenolic resin and, secondly, components of other resins on the market likely to be used in mines. In most of the cases examined, the maximum polymerisation temperatures obtained were lower than those measured for the resin/catalyst mixture, in the same operational conditions.

Changes in the resin-catalyst proportions

Laboratory tests were carried out to examine how a change in the volumetric resin/catalyst ratio affected the maximum polymerisation temperature. The tests showed that for a certain type of phenolic resin the maximum polymerisation temperature, measured on a volume of 800 ml of resin,

may be increased when the resin/catalyst mixture involves volumetric proportions of 2/1 of 4/1 rather than 1/1.

Influence of water

According to the laboratory tests, the presence of water tends to reduce the maximum polymerisation temperature of the phenolic resins used by a few degrees.

Influence of the **initial** reagent temperature

Laboratory tests were carried out on 200 ml of mixture to demonstrate that the maximum polymerisation temperature of the phenolic resins tends to increase as the initial temperature of the reagents increases.

Influence of the volume injected

Tests were conducted to investigate how the volume of resin injected affected the maximum polymerisation temperature. For a given type of phenolic resin, the maximum polymerisation temperature measured for a mixture with a volumetric ratio of 1 to 1 can increase by about 10 degrees if the volume changes from 200 ml to 10 litres, under the same operational conditions.

In laboratory tests carried out on volumes between 200 ml and 10 litres of a resin/catalyst mixture the initial temperature of which was 30°C, the measured maximum polymerisation temperature was of the order of 90-98°C. By comparison, the polymerisation reaction of the polyurethane resins involved in incidents occurring in mines led, in laboratory tests on small quantities (a few decilitres) and for an initial product temperature of the order of 25°C, to measure maximum temperatures above 150°C.

On the basis of the foregoing, the risk of coal overheating as a result in a rise in temperature following the introduction of the phenolic resins tested does appear to be less.

Risk of self-heating of coal

Tests were carried out by INERIS to evaluate the capability of phenolic resins to cause self-heating of coal as they polymerised.
These tests were conducted on coal encapsulated in a large volume of phenolic resin (about 80 litres) using a procedure already applied for other consolidation resins [3]. The test was done on one of the most reactive coals from Lorraine, crushed to a particle size of 200 µm, the initial temperature of which was previously raised to 40°C. The test was done on a mixture of the two resin and catalyst components in the volumetric proportions that give the highest polymerisation temperature according to the results of laboratory tests. The principle of the test is shown in figure 5 hereunder :

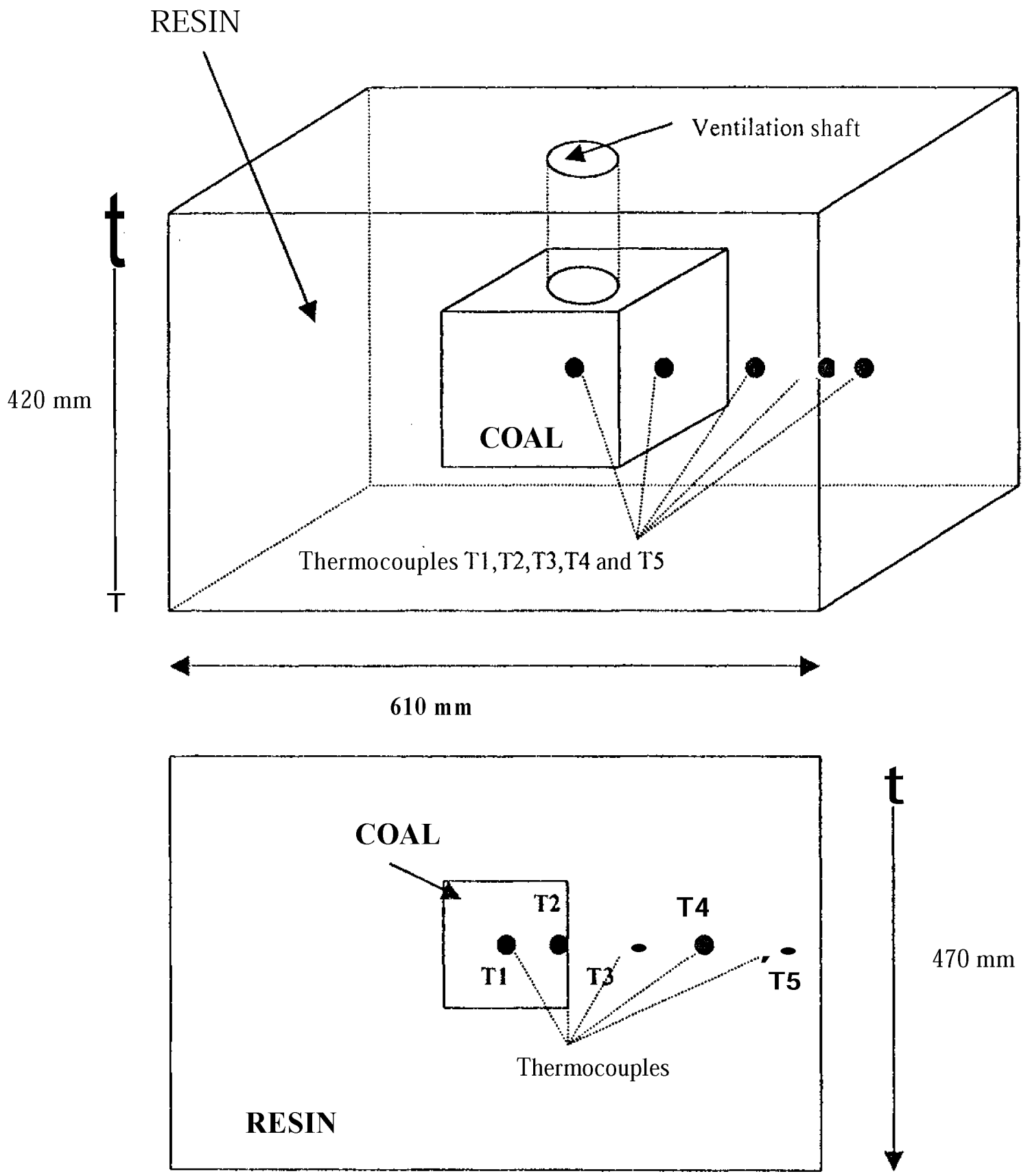

Figure 5. Coal Self-heating test

INERIS observed no ignition of the coal under test under the conditions of this trial.

A test similar to that described above was carried out by INERIS on a Lorraine coal preheated to an appreciably higher temperature than that of virgin ground [4], to simulate circumstances in which the resin, while polymerising, is in contact with coal in which the self-heating process has already begun.

Having regard to the tests conducted by INERIS on Lorraine coals an initial temperature of the coal of the order of 70°C was adopted.

This latter test was carried out on mixtures of the two resin and catalyst components in the most penalising volumetric proportions (ratio corresponding to a degraded situation) and on a one-to-one ratio (as recommended by the supplier).

INERJS observed no ignition of the coal under test under the conditions of this test [4] or for either of the two volumetric ratios of mixture tested.

In any event, these considerations are obviously meaningful only insofar as the conditions comply with the supplier's recommendations (1/1 mixture, use exclusively by injection, in limited volumes, ...).

Risk of gas ignition

The issue here is the risk of ignition of any gas present inside the cracks into which the resin is injected while polymerisation is going on. The main flammable ingredient of firedamp – methane - has a self-ignition temperature of the order of 600°C [5].

Other flammable gases such as ethane or propane have minimum self-ignition temperatures of around 500°C [5]. These values are considerably higher than the maximum polymerisation temperatures of the resins investigated during the laboratory tests done. Thus in the light of the tests carried out so far, direct ignition of gas has a result solely of the polymerisation of phenolic resins can be disregarded.

Risk of reaction with gases present in the rock

In view of the fact that formaldehyde - a highly reactive gas - is liable to be released during the polymerisation of phenolic resins, the question here is to consider the risk of reaction with gases that may be present within the rock. According to the literature [6], reactions between formaldehyde and alkanes have been observed only with hydrocarbon molecules of molecular weight equal to or higher than that of propane. It may be noted that these reactions, which can lead to the formation of molecules containing alcohol groups, are characterised by relatively slow kinetics and have been observed only in the presence of catalysts based upon organic peroxides. Also, in view of the fact that the quantity of alkanes with a molecular weight equal to or greater than that of propane in fire damp is relatively low, it is unlikely that the exothermic nature of the polymerisation reaction of phenolic resins will be modified significantly as a result of this type of secondary reaction. In the light of the above, it seems likely that the gases present in the rock will not have any significant influence on the polymerisation reaction of phenolic resins.

Moreover phenolic resins, once cured, are relatively inert chemically [7], and are unlikely to react with the principal gases present in firedamp.

Finally, the operator plans to carry out laboratory tests to investigate the interaction between methane and a phenolic resin during polymerisation.

Risk of reaction with local minerals

The question here is to consider the risk of an exothennic reaction between the products used and minerals likely to be present in the rock.

This possibility cannot be set aside since the strong acids used as hardeners for resins are likely to react with limestone rocks giving rise to a release of heat and emission of carbon dioxide.

Also minerals such as pyrite are known to react with water in an exothennic manner, notably when they are in a powdery state. Since the reagents used for curing phenolic resin are in an aqueous solution, the operator has had a laboratory test carried out in order to characterise the reactivity of the phenolic resins used and of its basic ingredients with finely divided pyrite.

CONCLUSION

From the hazard analysis carried out on the entire phenolic resin injection process investigated (from arrival of the reagents at the pithead until they are used for ground consolidation), it seems that any hazard arising from the use of phenolic resins will occur essentially during the phase of polymerisation of the resin.

On the basis of laboratory tests, it appears that the rise in temperature resulting from the polymerisation of phenolic resins is appreciably less than that observed during the use of polyurethane resins under comparable conditions.

This increase in temperature does not seem such as to give rise to self-sustaining heating of the coal, as part of an operating procedure that complies notably with the supplier's recommendations (1/1

mixture, use exclusively by injection, ...) and so long as the preventive and protective measures proposed are applied.

These measures involve:

- Setting out the responsibilities of the different people involved in the process of using phenolic resins, starting from receipt of the reagents through to the injection of the resins into the rock. Indeed it is essential that there should be no "fuzzy areas" between any two successive operations of the above process for which nobody feels directly responsible.
- Preparing suitable written procedures, setting out in detail the routines to be followed for the application of phenolic resins, from the time they arrive at pithead until they are injected into the ground.
- The ways and means (both stationary and mobile) of fighting fire at the surface and in the mine.
- The collection facilities available on the site for containing any uncontrolled release of products.
- Checking that the reagent containers are generally in good condition, as well as their labelling and sealing.
- Taking samples systematically from each batch of injection products supplied, with a view to carrying out tests on the physical and chemical properties, the composition and reactivity of the products (measuring the viscosity of each reagent used, measuring the maximum polymerisation temperature of the resin in the laboratory, measuring the degree of expansion during polymerisation of the resin, and the acidity of catalysts).
- Proper management of empty containers at worksites.
- Management of storage areas in the mine.
- The stability of the workstations.
- Utilising a single type of phenolic resin at any one time in the mine.
- Training operators and making them aware of the hazards related to the products used.
- Keeping resin ingredients at a temperature of less than 30°C.
- Checking that safety devices operate correctly (non-return valves, relief valves, hoses, unions, control valves, etc.).
- Identifying and inspecting reagent transfer pipes.
- Communications between the operators responsible respectively for pumping and injection into the rock.
- Ensuring that the injection of phenolic resins is strictly limited to normally fissured rock (excluding collapsed or shattered rock).
- Following the recommendations set out by the resin suppliers.
- Quantifying the liability of coal to self-heating for all the panels where the phenolic resins will be used, to verify that it is not significantly higher than that of the specimens on which the tests were carried out.

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