

THE RELEASE OF HYDROGEN SULPHIDE FROM
FORMED SOLID ELEMENTAL SULPHUR

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INTRODUCTION

By far the major portion of elemental sulphur exported from Western Canada is in solid prill, pellet, granule or slate form made from Claus recovered liquid sulphur. This sulphur contains small but significant residues of the hydrogen sulphide from which it, in turn, was made. This residual hydrogen sulphide can be in the form of dissolved gaseous H_2S or chemically combined as hydrogen polysulphide (H_2S_x). The equilibrium relationship between these two forms and methods of measurement of each have been the subject of various articles in the Quarterly Bulletin over the past several years ¹⁻⁴.

The residual level of hydrogen sulphide and the H_2S/H_2S_x ratio in Claus sulphur depends on a number of factors such as H_2S content of the acid gas feed to the sulphur plant, front end reaction furnace temperature and operating characteristics of the catalytic Claus units in the reaction train. The total ($H_2S + H_2S_x$) level of residue in the liquid sulphur feed to the forming process can again be influenced by the length of time and the temperature at which the liquid sulphur was held in storage in either the rundown pit or storage tanks. In some cases actual degasification of the liquid sulphur is attempted using various spraying, sparging or agitation techniques. While these methods are reasonably effective in removing the dissolved gaseous H_2S portion of the total hydrogen sulphide content, they are of little benefit as far as reducing the H_2S_x or hydrogen polysulphide content of the sulphur. This requires decomposition of the H_2S_x component to the free H_2S and sulphur, and can be a relatively slow process unless a catalyst is present. Again this topic has been dealt with at length in an earlier Quarterly Bulletin article ⁵.

Because of the complexities noted above it is hardly surprising that the level of total hydrogen sulphide in the Claus liquid sulphur feed to a forming plant is somewhat variable. We have previously measured values as high as 500 ppm and as low as 20 - 30 ppm but as a normal average,

values in the 80 - 150 ppm range are most common. As much as half of this total hydrogen sulphide content may be dissolved gaseous H_2S which, like most other gases dissolved in liquids, will be partially released from the liquid phase upon solidification. Thus the process of forming liquid Claus sulphur feed into solid particulate is itself an effective method of partial "degassing". Nonetheless, the freshly formed solid sulphur of whatever geometry and internal structure will still contain some residual hydrogen sulphide likely to be predominantly in the H_2S_x or polysulphide state.

It is the slow decomposition of the residual H_2S_x trapped in the formed solid sulphur that serves as a new source of gaseous H_2S within the solid sulphur matrix. This H_2S must then diffuse to the surface of the solid form before it can escape to atmosphere. It is this process which is the subject of our quantitative study that is reported in this paper.

QUALITATIVE EVIDENCE FOR H_2S RELEASE FROM FORMED SULPHUR

The industry's experience with slated sulphur is much greater both in terms of tonnage and time than it is with the newer premium product prills and granules. This slate experience leaves little doubt that the phenomenon described in the Introduction is, indeed, a real one. Through most of the 1970's large tonneages of Claus recovered sulphur were slated and stockpiled at Western Canadian sour gas plants. Rupturing a freshly made slate under the nose would seldom yield the telltale rotten egg smell of H_2S . The same exercise with a well aged slate (say one year old) would likewise yield no odor. However, a slate of intermediate age (say 2 - 3 months) would yield a distinctive H_2S smell when broken.

These qualitative observations are in keeping with the processes described in the Introduction. The fresh slate has recently been well degassed by the liquid to solid phase change during forming. Hence little free H_2S gas is present within the solid matrix and thus no smell is detected on rupture. After a month or two, however, sufficient of the polysulphide has decomposed to yield a detectable amount of occluded gaseous H_2S within the internal pores and crevices of the solid form

which is released on rupture. The polysulphide decomposition process, even uncatalyzed, will have largely proceeded to completion after one year and the produced gaseous H_2S will have diffused to the surface of the solid form and escaped to atmosphere. Thus rupture of a year old slate will release little or no gaseous H_2S .

Similar experiences involving some of the new premium products have been noted. A bag or vial of newly formed prills, kept sealed for two or three weeks will release a very readily detectable level of H_2S when opened or broken. It must be emphasized that the rate of release of H_2S from the solid forms is very slow and under normal, open air conditions natural dispersal of the released H_2S prevents the ambient level from ever exceeding even the lowest environmentally acceptable limits. Indeed a good organic bog or swamp probably releases as much H_2S on a continuous basis as a prill stockpile might do over a limited period of a few months. Furthermore, the amount of H_2S released will vary depending on the original total H_2S content of the liquid sulphur feedstock to the forming process and this, in turn, will vary from plant to plant.

The Type of Formed Sulphur Studied

Since 1980 there has been a steady increase in the amount of Western Canadian sulphur formed into spherical types such as prills and granules. Present capacity in these categories now exceeds three million tonnes/annum. There has been a corresponding de-emphasis of slate production although a significant portion of solid formed sulphur moving to export tidewater points on the West Coast as of early 1983 was still in the slated form. Nonetheless the spherically formed types are likely to continue to represent an increasingly large proportion of the total formed sulphur exported and among these spherical types the Polish Air Prill is the most common form. Accordingly, this form was selected as the material for the H_2S release study reported here.

EXPERIMENTAL METHODS EMPLOYED

How can the H_2S release be measured? Two techniques were utilized - gas chromatography for measurement of developing H_2S concentrations in

the gas phase and infrared spectroscopy for measurement of the decreasing H_2S and H_2S_x concentrations in the prills.

The two litre prill-containment vessels used in this study were three neck, all glass flasks. One neck was used to purge the vessel with nitrogen and the stopcock was kept closed thereafter. It is important to ensure that oxygen (air) is excluded if accurate H_2S concentration measurements are to be made since over the long periods of time of the experiments, it is possible that some H_2S may be oxidized especially if light and surface catalysts are operative. The large neck in the middle was used to introduce the sample usually 100 - 125 g of freshly prilled sulphur. The third neck was sealed by a rubber septum through which a syringe needle could be introduced for removal of gas samples for analysis. Eight containment vessels were used. Four of these were loaded with samples of sulphur containing a higher initial H_2S concentration than the samples in the other four. All samples were kept at room temperature.

A Varian 3700 gas chromatograph was used to analyze 100 μl gas samples removed from the containment vessels over a three month period. A Poropak QS column at 70°C was used and output data was reduced by a Varian Aerograph CDS 111 chromatography data system to yield H_2S concentrations in the gas phase expressed in ppm.

The declining H_2S and H_2S_x content of the solid phase was followed by sampling a large reservoir of the same prills used in the glass containment vessels but held separately in large plastic buckets kept sealed with film between samplings. This method avoided massive disturbance of the gas phase composition in the glass containment vessels that would have resulted from attempting to remove solid samples from these containers. Although it would have been ideally preferable to examine the actual prills from which the H_2S had been liberated, we do not believe that the parallel sample technique used in this work introduced any significant errors at the level of accuracy required.

Infrared analyses on the solid were performed several times over a three month period using the ASR Infrared Analyzer and procedures described previously ⁴. About 70 g of prills was removed from the surface of each bucket reservoir for each analysis, except for a few analyses of more

deeply buried prills taken from several inches below the surface. It must be emphasized that the prills were melted and the spectra obtained were those of the resulting liquid. Every effort was made during the melting process to ensure that any gaseous H_2S released was contained within the system that was loaded into the infrared cell. Nonetheless we expect that some gaseous H_2S contained within the pore structure of the prills may not have been redissolved into the liquid on melting and may have escaped to atmosphere.

Analyzing both the solid and the gas allowed a simple mass balance to be done - H_2S lost from the prills should appear in the gas phase. As discussed more thoroughly in the "Discussion" section, the discrepancies between the two sets of data can be explained in terms of a more complicated mechanism for H_2S release from solid sulphur.

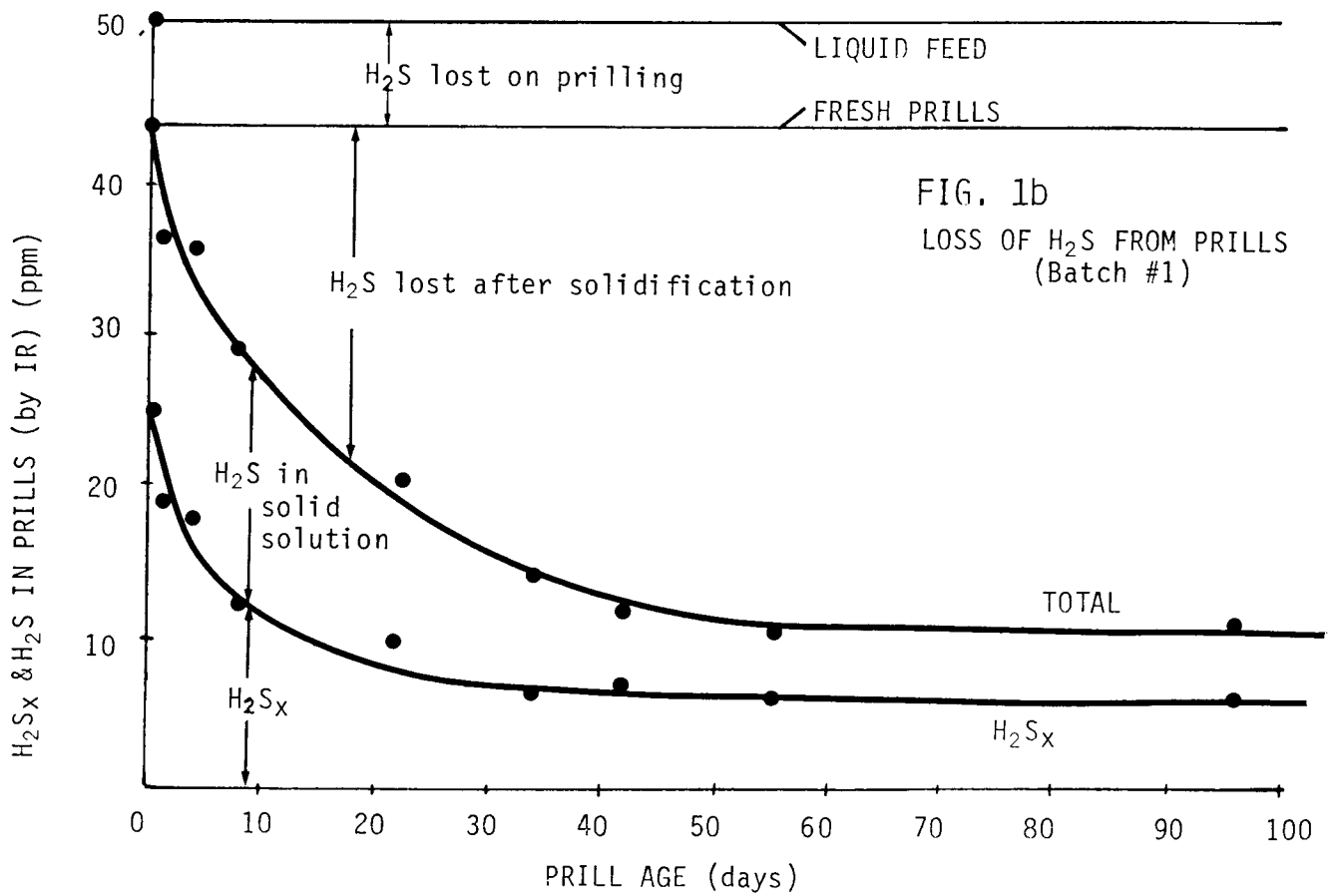
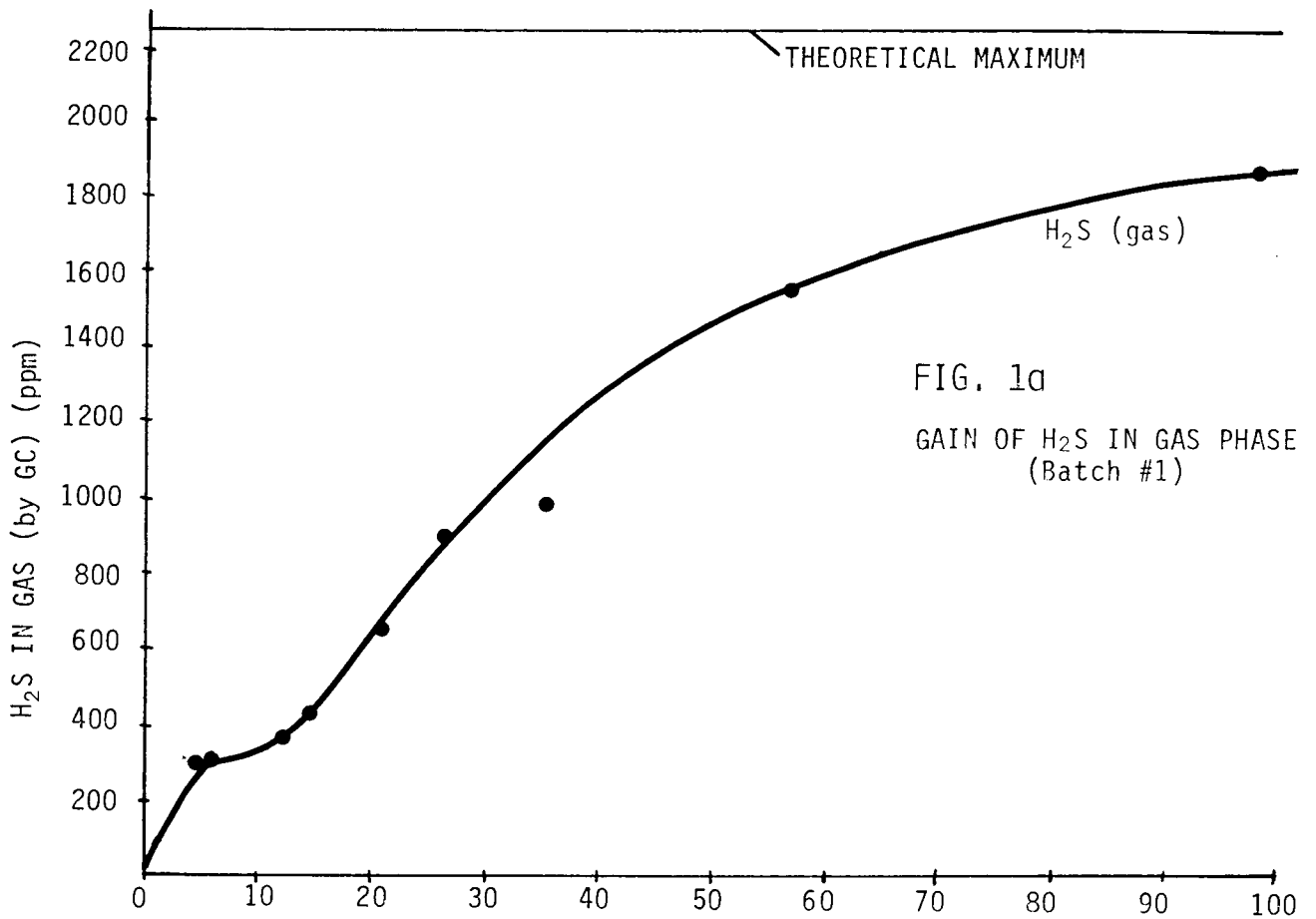
RESULTS AND INTERPRETATION

Batch #1 - Higher Initial H_2S Concentration

The two prill samples or batches of product were taken from the prill tower product conveyor at different times. Batch #1 was made from a liquid feed that was analyzed and shown to contain 50.8 ppm total H_2S . The fresh prills made from this feedstock were analyzed as soon as possible and were shown to contain 43.8 ppm total H_2S . As noted previously the act of solidification itself results in some loss of gaseous H_2S from the sulphur. The rate at which the Batch #1 prills decreased in total hydrogen sulphide content ($H_2S + H_2S_x$) and in the separate H_2S_x component is reported in graphical form in Fig. 1b. The rate of liberated H_2S build-up in the gas phase above the prills is plotted in Fig. 1a.

The ppm values on the y-axes deserve comment. One may wonder how only 43.8 ppm total initial H_2S in the solid can give rise to over 1500 ppm in the gas. The answer lies in the relative densities of the solid and the gas. Each vessel contained over 100 g of sulphur but only about 2 g of vapour. Thus, a given amount of H_2S forms a much greater weight fraction of the vapour than of the solid.

The theoretical maximum shown in Fig. 1a is calculated on the assumption that all of the H_2S and H_2S_x initially contained in the prills



is released to the gas phase as H_2S . As seen in Fig. 1b this has not happened after 100 days and the theoretical maximum is not reached.

By measuring both the rate of loss from the solid and the rate of gain in the gas phase a mass balance calculation can be performed. After normalizing the data for the same weight of prills the results of the mass balance calculations can be plotted as in Fig. 2a. Here we see the ppm content of the gas phase as measured directly (repeat of Fig. 1a) compared with the calculated H_2S content of the gas phase based on the loss of total $\text{H}_2\text{S} + \text{H}_2\text{S}_x$ from the solid phase as measured by infrared. It is clearly seen that there is no mass balance. The loss from the solid phase is not all appearing in the gas phase? Why?

We believe that the difference or lack of mass balance is due to the amount of H_2S gas trapped in the porous solid matrix of the prill which is lost during the melting process required for the IR analysis. Indeed if the difference between the measured gas phase H_2S content and that calculated from the IR measurements on the remelted prills is plotted as in Fig. 2b, we see that the difference increases to a maximum at around 18 days and then slowly diminishes to essentially zero at long storage times. This behaviour is in keeping with the process of relatively rapid saturation of the pore structure within the prill as ageing and H_2S_x decomposition occurs initially, followed by slow diffusion out of the pore structure to atmosphere. This is precisely the same observation that was made qualitatively with slate; that fresh or old slates do not smell when broken but intermediate age solidified sulphur does release detectable quantities of H_2S trapped in the porous matrix. The time scales will, of course, be different for prills and slates because of the different geometry.

We should comment also on the apparent initial hesitation in build-up of H_2S in the gas phase. We suggest that this is another manifestation of the pore saturation process used to explain the apparent lack of mass balance. After an initial relatively rapid degassing of the outer layers of the prill structure, leading to the establishment of a 300 - 400 ppm H_2S level in the gas phase, there is a "pause" in further H_2S build-up

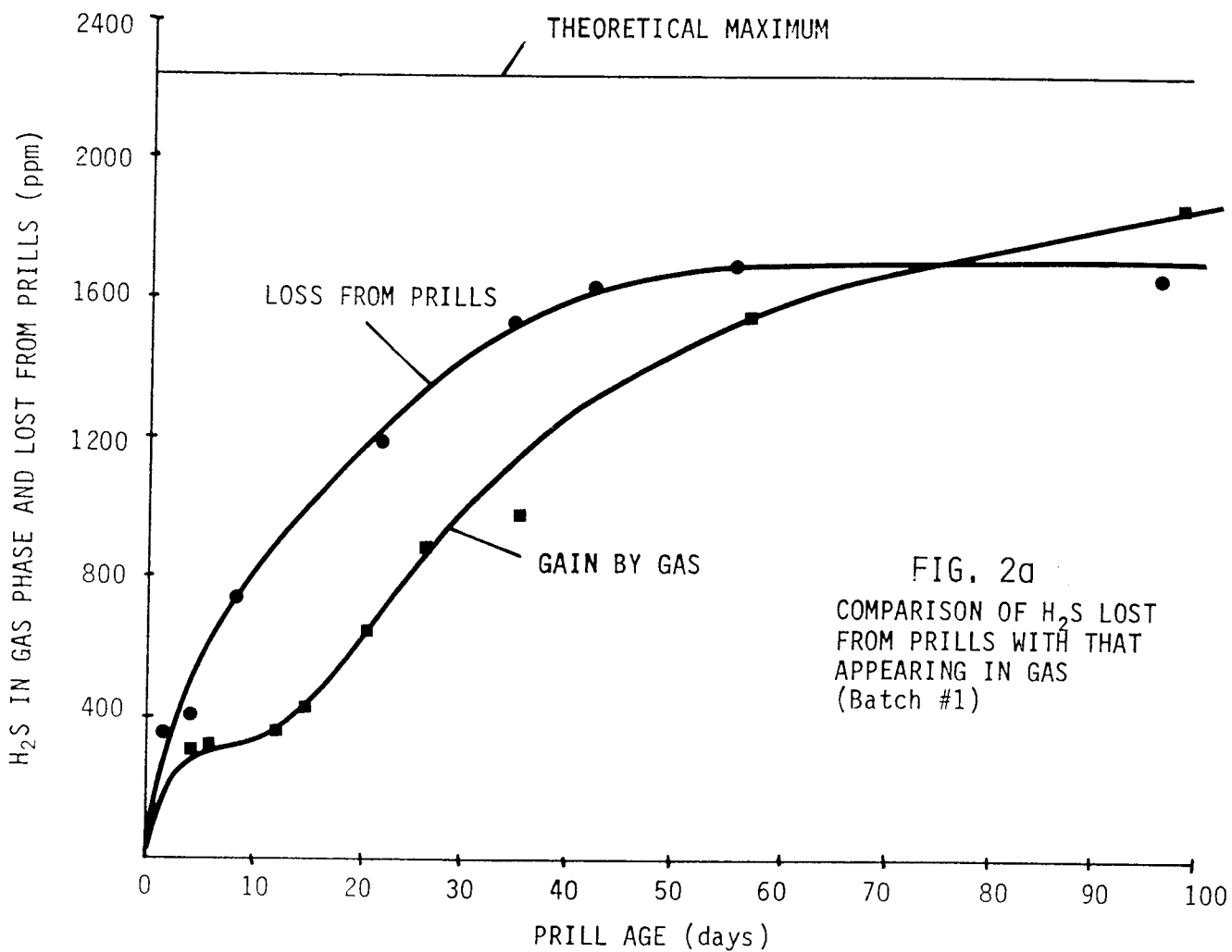
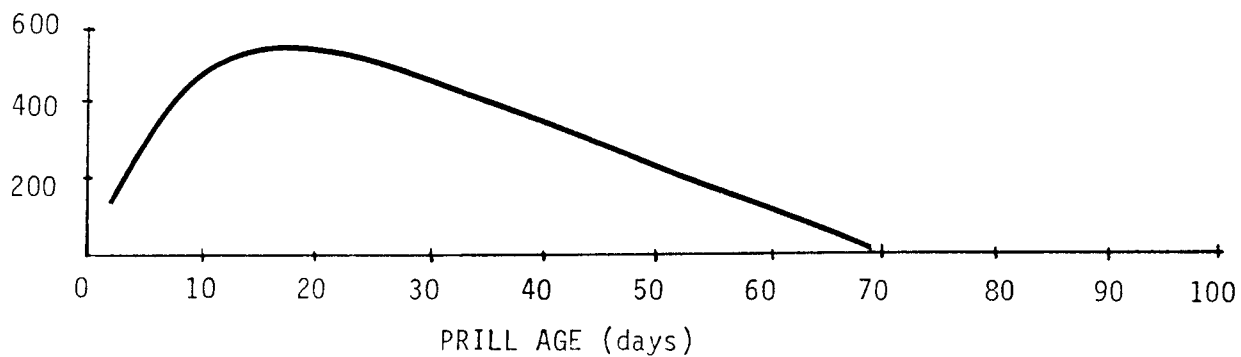


FIG. 2b
H₂S IN POROUS MATRIX OF PRILLS
(by difference)



in the gas phase because of the relatively slow resaturation of the pore structure with newly formed H_2S from the decomposition of H_2S_x in the solid. This appears to take as long as 14 days after prill formation.

Batch #1 - Surface vs Buried Prill Degassing

The IR analysis of prill material as a function of time, reported and discussed above, was performed on samples removed from the surface of the large bucket reservoir of material kept in storage. In practice, however, by far the bulk of prill material in storage will not be surface material exposed to atmosphere but will be deeply buried beneath the surface of the stockpile. Thus it was important to determine whether there was a significant difference in the rate of release of H_2S from prills buried beneath the surface and those at the surface.

This was carried out by performing IR analysis of prills from within the bulk of the bucket storage as well as at the surface as a function of time. The results are shown in Fig. 3. The results leave little doubt that the rate of release decreases markedly when the prills are not at the surface interface between the sulphur and atmosphere. We believe that this again is the result of a series of coupled equilibria involving build-up and saturation of the internal pore structure and the ease with which the H_2S in the pores can diffuse to and be dispersed in the atmosphere.

Batch #2 - Lower Initial H_2S Concentration

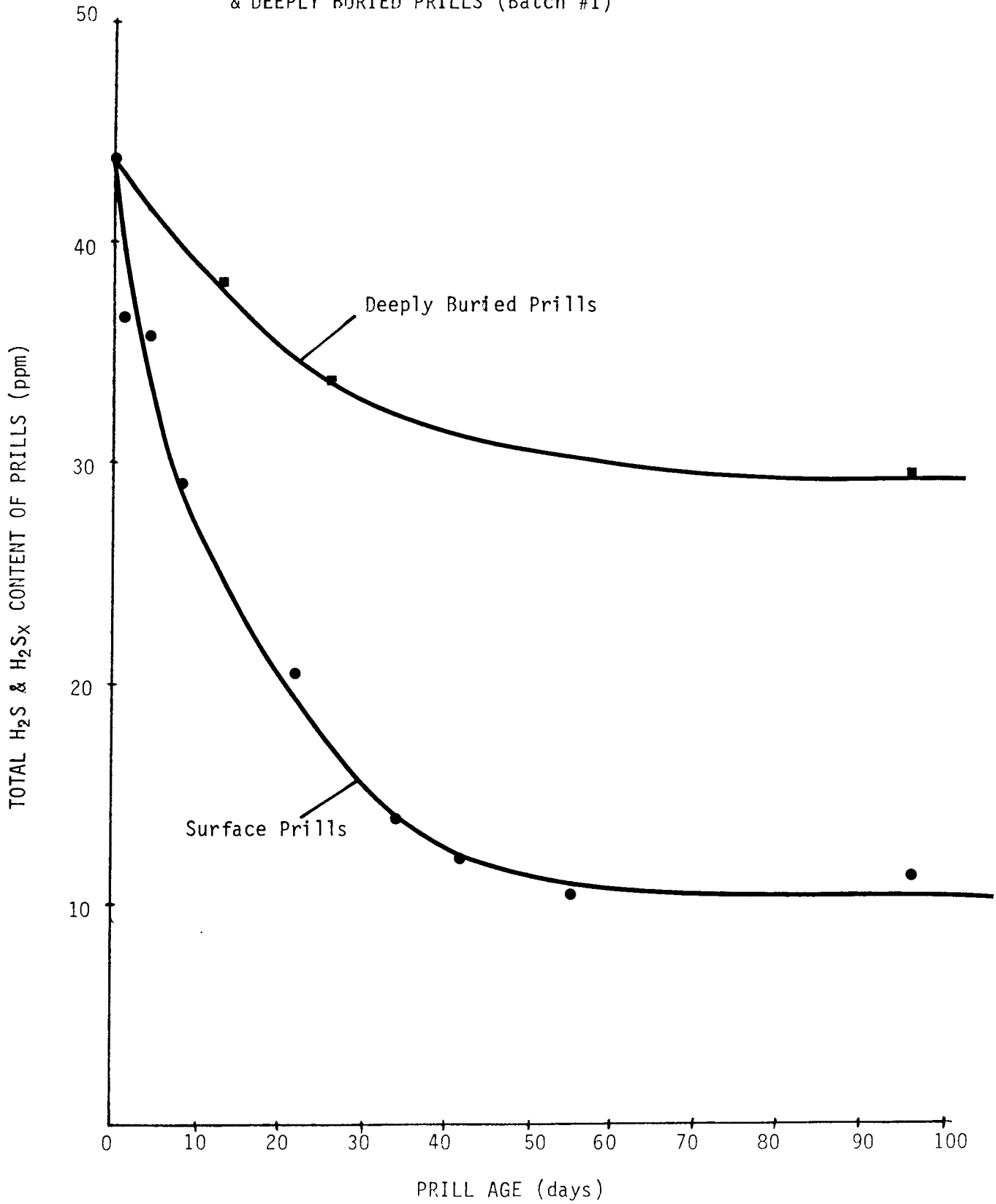
Samples from Batch #2 were treated in the same manner as those from Batch #1. The feed sulphur for Batch #2 had a lower total H_2S content and a slightly lower proportion of this in the form of H_2S_x .

Comparing Figs. 4a and 4b with 1a and 1b shows very similar patterns. The major difference, as far as the solid is concerned, is the essentially total disappearance of " H_2S in the solid solution" seen for Batch #2. However, it should be recognized that, at levels below 5 ppm, we were operating very near the minimum detection level for H_2S so experimental errors are large in relative terms.

The mass balance calculation was again performed to compare measured release of H_2S into the gas phase with that calculated from the IR analysis

FIG. 3

COMPARISON OF TOTAL H_2S AND H_2S_x LOSS FROM SURFACE PRILLS
& DEEPLY BURIED PRILLS (Batch #1)



of total H_2S and H_2S_x content of the prills. The results are plotted in Figs. 5a and b. The general format is the same as that noted in Figs. 2a and b with the porous matrix saturation level being reached at approximately the same time. There is some suggestion, however, that the amount of H_2S in the pores may not drop to near zero after 3 months as was observed in Batch #1. This may be related to the lower total initial H_2S_x level and thus a lower driving force to displace the pore entrapped H_2S but it should also be remembered that at these very low levels of total H_2S we are approaching the limits of instrumental detection and errors may be significant in relation to the values measured. These errors in IR measurements are then greatly magnified when converted into gas phase ppm equivalents.

Fig. 6 shows a comparison of the loss of H_2S from surface prills in Batch #2 with the loss from more deeply buried prills. Again, the evidence is clear that prills in the interior gave off H_2S much more slowly than those at the surface.

DISCUSSION

The Mechanism of H_2S Release from Prilled Sulphur

The experimental evidence acquired in this study permits the construction of a mechanism or series of steps describing the release of hydrogen sulphide from prilled elemental sulphur and possibly from all forms of solid sulphur.

It was established as early as 1966⁶ that there were two distinct forms of H_2S in liquid sulphur - H_2S which was truly dissolved and H_2S which had reacted to form H_2S_x . It is generally conceded that H_2S_x cannot be released from liquid sulphur directly and this must also hold for the solid. In order for H_2S_x to be released (A - see Fig. 7) it must decompose to H_2S (B) and sulphur. Release of dissolved gaseous H_2S from liquid sulphur to the atmosphere is a relatively simple process because of the mobility of the liquid. However, the structural rigidity of the solid complicates the diffusion process. H_2S (B) released in the interior of a solid mass of sulphur becomes trapped in the porous matrix between the crystals (C). From there it must migrate to the surface of the prills in

FIG. 4a
GAIN OF H₂S IN GAS PHASE (Batch #2)

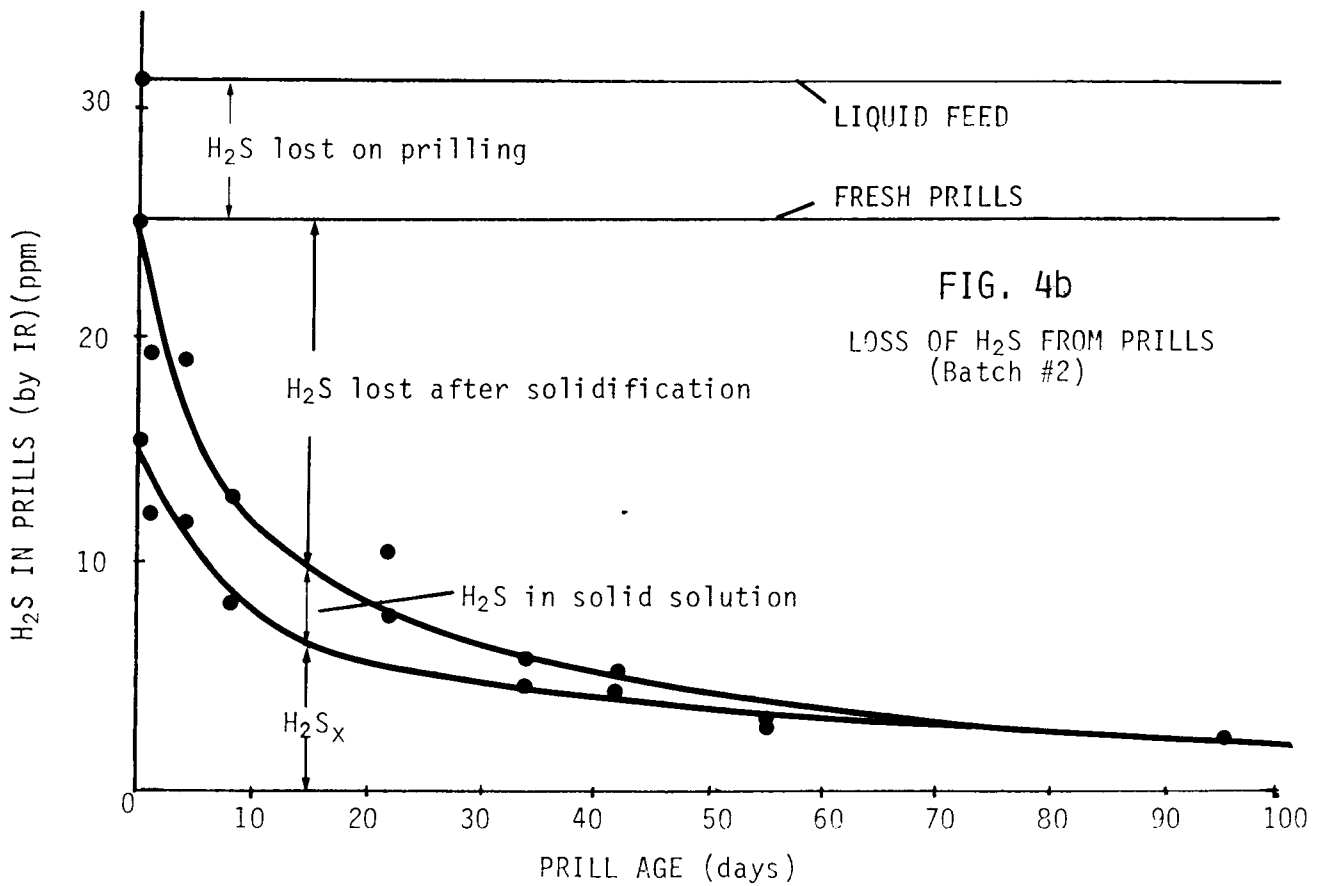
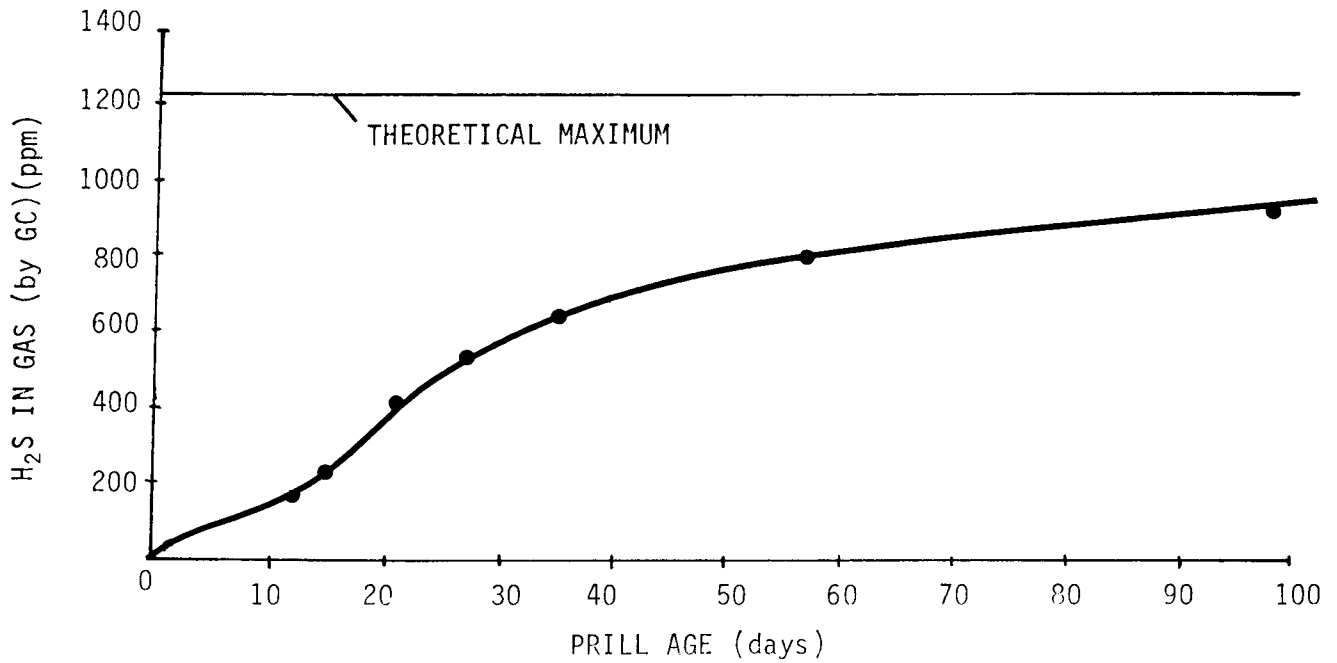


FIG. 4b
LOSS OF H₂S FROM PRILLS
(Batch #2)

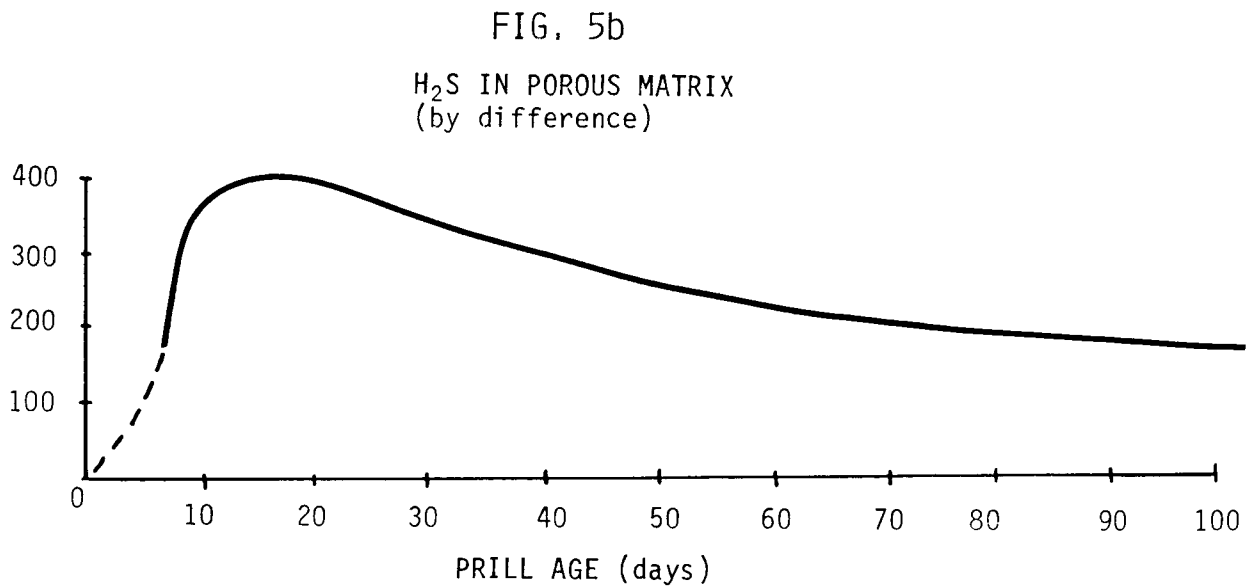
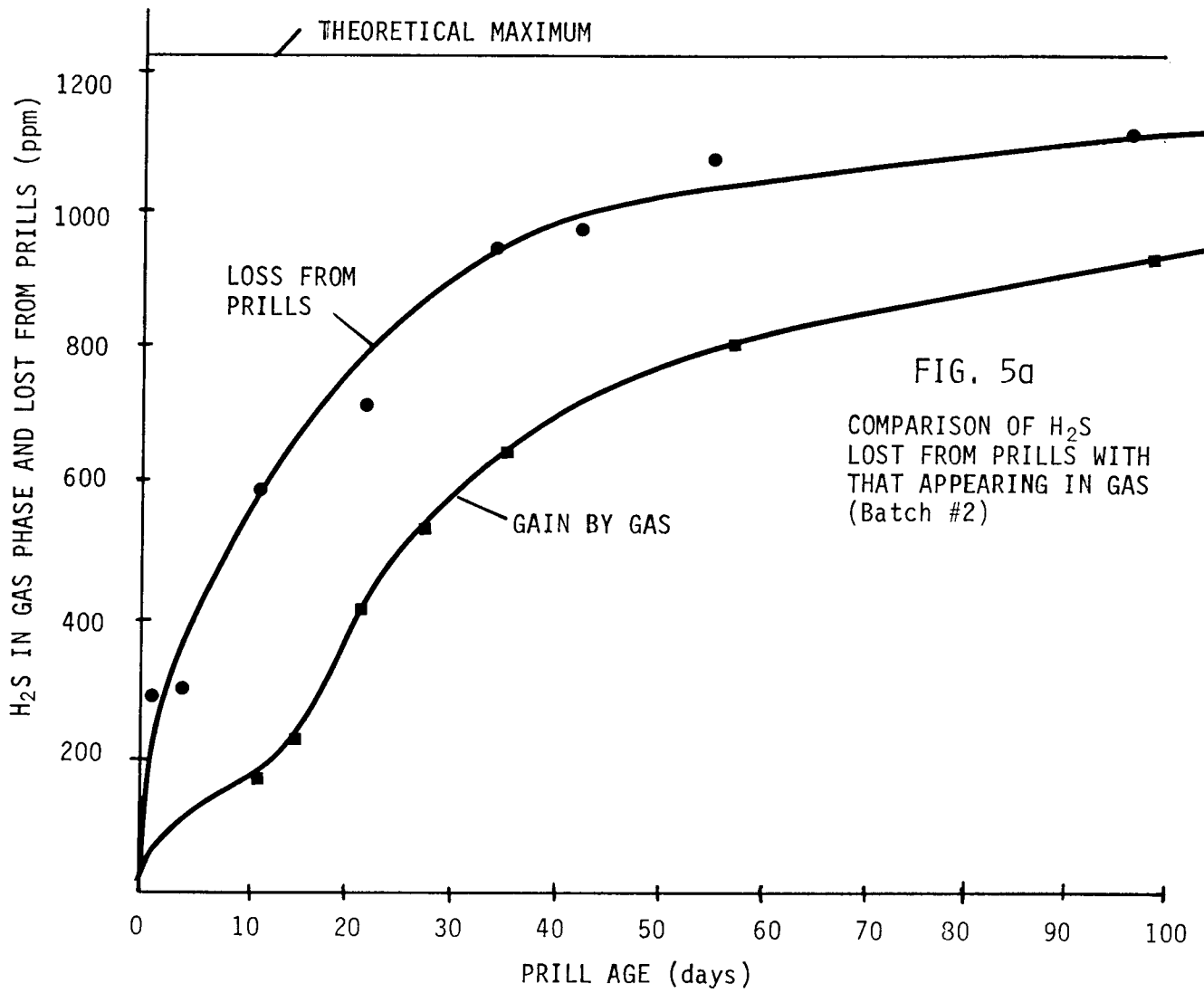
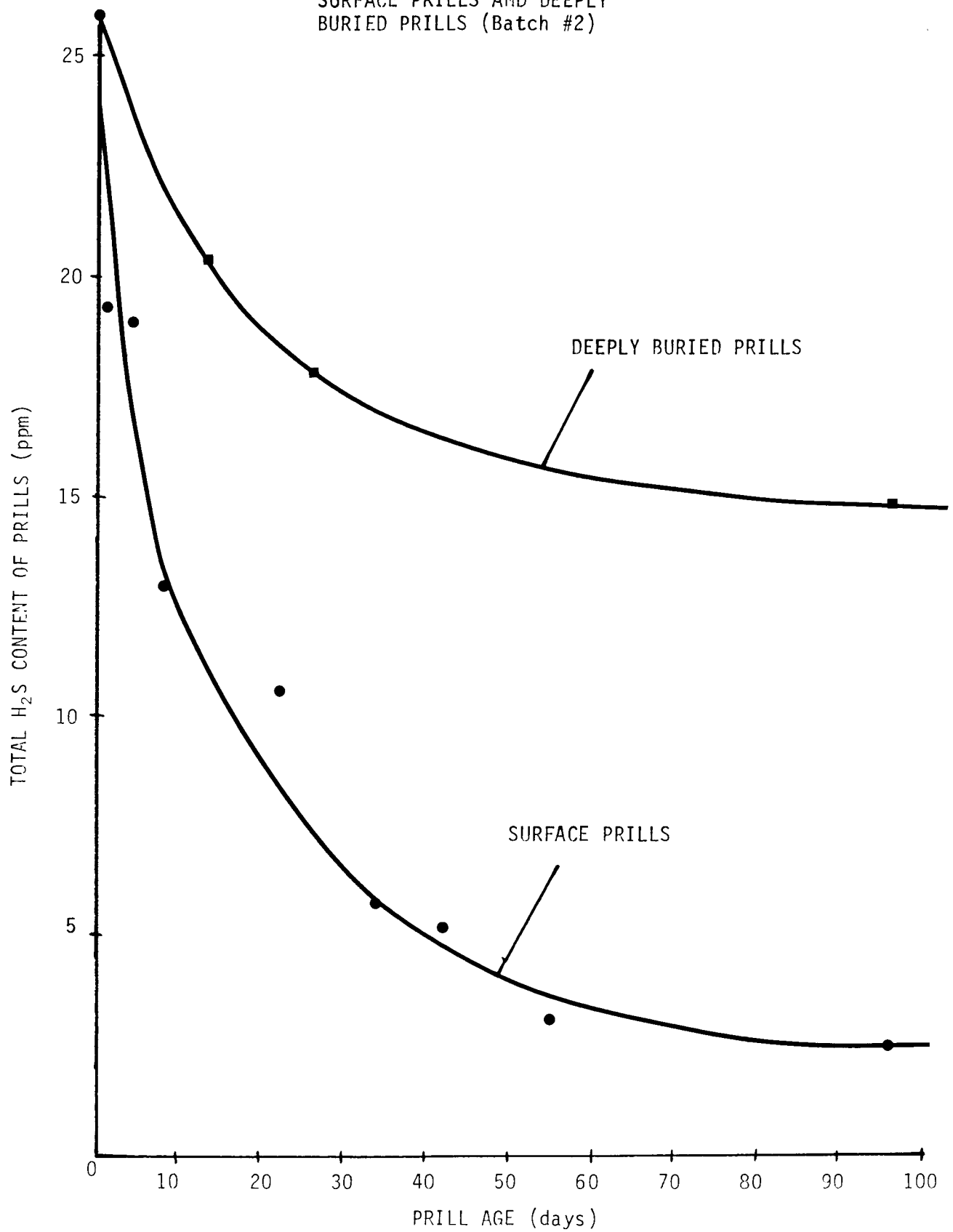


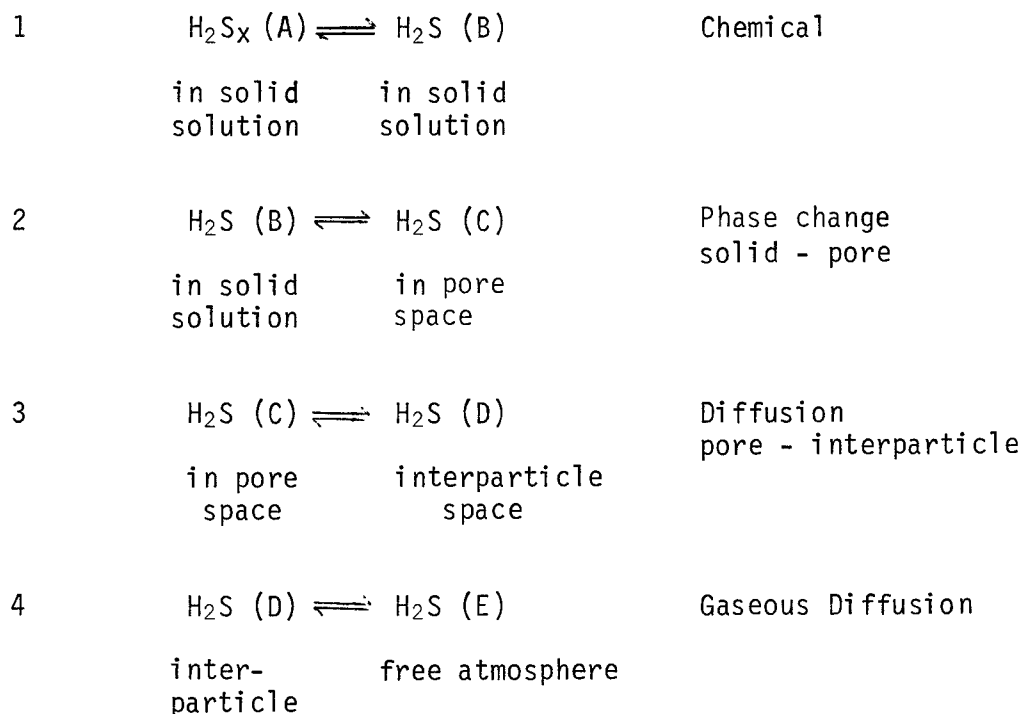
FIG. 6

COMPARISON OF H₂S LOSS FROM
SURFACE PRILLS AND DEEPLY
BURIED PRILLS (Batch #2)



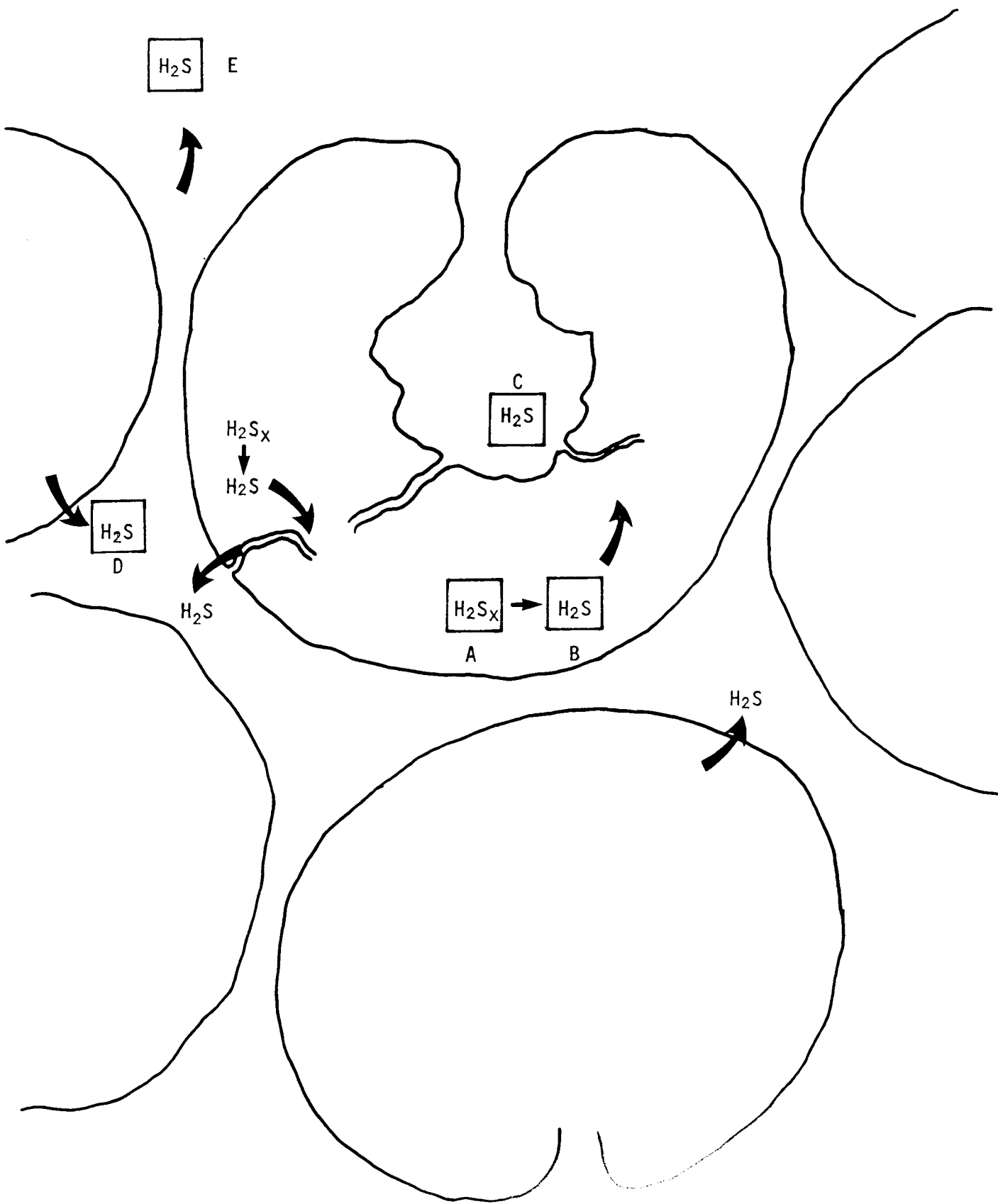
the bulk but then it can be trapped in the spaces between the prills in the bulk (D). Migration through these spaces to the surface interface finally allows the H₂S to escape from the sulphur to atmosphere (E).

We propose that these various steps coupled are in a series of equilibria that may be represented as follows (see also Fig. 7):



All of these steps are interconnected and, we believe, necessary in order to explain the experimental data reported. IR analyses of the solid (after melting) showed the amounts of H₂S_x (A) and H₂S (B) in solid solution. GC analyses of the gases in the containment vessels gave direct measurements of the H₂S in the atmosphere (E). The H₂S not measured by either technique (i.e. that amount required to make up the original total H₂S content of the prills) is that trapped within individual prills (C) or between prills (D). All of this is lost when solid sulphur is melted for infrared analysis and represents the shortfall in the mass balance shown in Figs. 2b and 5b.

FIG. 7
SCHEMATIC ILLUSTRATION STEPS
IN RELEASE OF H₂S FROM PRILLED SULPHUR



All the processes shown in the mechanism are reversible. This explains why deeply buried prills degas more slowly than surface prills. The build-up of H_2S in the spaces between the prills allows reabsorption of H_2S into the prills. Backing up any one process in the series causes concentrations of earlier intermediates to build up, eventually resulting in all prior processes being effectively slowed down. In effect, the rate of loss of H_2S from a large batch of prills becomes dependent on the rate of diffusion of H_2S between the prills to the surface. Looking at this from the opposite point of view, the slower degassing of prills in the interior lends credence to postulation of H_2S trapped between the prills as a separate intermediate in the mechanism.

What are the Implications for the Storage and Handling of Formed Sulphur?

Though this study concentrated on Polish Air Prills, the results and recommendations arising from it should have general applicability to all sulphur forms. Qualitative differences between forms could arise from different surface areas for a given weight of sulphur, i.e. different particle sizes.

It is clearly desirable to use a liquid sulphur feed with as low a total H_2S concentration as possible. The maximum gaseous H_2S concentrations reached in the enclosed vapour space above the formed sulphur was significantly lower (1100 ppm) when the original liquid feed contained only 30 ppm total H_2S (Fig. 4a) than that (1800 ppm) reached when the feed sulphur contained 50 ppm (Fig. 1a). It must be emphasized that these H_2S accumulations were in a completely sealed system and occurred over several months of prill ageing. Nonetheless they do illustrate that undesirable vapour phase levels of H_2S can be generated even when the initial total $H_2S + H_2S_x$ content of the sulphur is relatively low. The relationship between eventual gas phase concentration and initial sulphur content is similar to that observed with degassing of liquid sulphur in tank cars discussed in a separate article in this issue of the Quarterly Bulletin.

Adequate ventilation of formed sulphur storage areas is therefore mandatory. The rate at which the H_2S is liberated to atmosphere is not such as to result in the effluent ventilating air exceeding regulatory limits for H_2S content as long as the H_2S is not allowed to accumulate. Any reasonable rate of air change (say four times daily) would normally be adequate to avoid undesirable build-up of H_2S but each situation can be evaluated on its own merits using the data provided in this paper to yield at least a "worst possible situation" type of scenario.

The H_2S release and necessary ventilating requirements have not been a consideration with slated sulphur heretofore since slate stockpiles were normally stored outdoors with abundant natural ventilation. Increasing efforts to maintain the formed product in a dry state, however, have led to an increasing tendency to store the formed product in bins, silos or even shed structures where adequate ventilation should be given careful consideration.

It is also worth noting that any H_2S build-up due to formed product degassing is not likely to even approach the explosion limit for H_2S /air mixtures which is in the region of 33,000 ppm and somewhat temperature dependent. Human toxicity levels, however, are much lower as illustrated in Table 1 and it is these values that are more likely to be approached in confined storage areas with poor ventilation.

The relatively slow but steady loss of H_2S from prills suggests that it may be desirable to ship aged rather than freshly formed sulphur. The older the sulphur is, the less H_2S there is to be released in containment vessels during shipping and the slower this release will be. Because the rate of loss is greatest soon after forming and then becomes progressively slower, there is more to be gained by allowing freshly formed sulphur to age, than by allowing further ageing for an already aged batch, i.e. the oldest available sulphur should be shipped first.

The results reported on the effect of depth of burial beneath the surface suggest two practical cautions. The first relates to rate of ageing and thus degassing in the stockpile. It would seem preferable to store formed sulphur with as great a surface area of exposure to atmosphere as possible and to avoid deep, columnar type storage vessels.

Table 1

H ₂ S LEVEL	SAFETY CONSIDERATION
0.13 ppm	Odour threshold (average individual)
10 ppm	Threshold Limit Values (TLV) - recommended maximum time - averaged concentration for a normal workday.
70 - 150 ppm	Slight symptoms after several hours exposure.
170 - 300 ppm	Maximum concentration that can be inhaled for 1 hour without serious consequences.
600 ppm	LD 50
> 1,000 ppm	Rapid death - respiratory paralysis
33,600 ppm	Lower explosive limit

This means that large shed type storage is preferable over silos. The economic disadvantages of large roof areas in shed structures, however, may make the silo type structure the preferred one. In these cases the possible accumulation of H_2S within the interprill spaces should be noted. Hydrogen sulphide is significantly denser than air and will not readily rise through the column of prills without a driving force. This might be provided by slow purging of the prill column with air but in any event care should be exercised in opening lower level delivery chute gates in any prill storage vessel to ensure that there has not been a build-up of released H_2S in these areas.

CONCLUSION

H_2S release from formed sulphur can occur over a period of months. The release is relatively rapid at first, becoming slower as the total H_2S content of the solid decreases. In unventilated areas, undesirable levels of H_2S can arise from sulphur containing relatively low total H_2S and H_2S_x . Sulphur on the surface degasses more rapidly than that in the bulk of a stockpile.

ACKNOWLEDGEMENT

The authors would like to thank Gulf Canada Resources Inc. for their cooperation and their personnel at the Strachan Gas Plant for their assistance in the initiation of this study. The contribution of Dr. G. Derdall to some parts of this work are also acknowledged.

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