

**Hazards from Pressure:  
Exothermic Reactions,  
Unstable Substances,  
Pressure Relief and  
Accidental Discharge.**

IChemE Symposium Series No. 102  
(16-18 June 1987)

**Discussion of Papers**

REPORT OF DISCUSSION

NOTES

1. Q/C means question or comment
2. R/A means response or answer by presenter
3. Name of author(s) actually presenting paper - normally the respondent
4. Affiliations, etc. appear in delegate list (obtainable from D.V. Greenwood)

SESSION 1 UNSTABLE SUBSTANCES (Chairman: N. Gibson)

Paper No 1: Grewer and Klais

Q/C (O. Klais) The fire in the Sandoz storage (1986) as reported in newspapers, was due to a propagating decomposition. The fire may have been initiated by accidental overheating of the reducing compound. Propagation of decomposition could have occurred for several hours without producing gas before an open fire developed.

Q/C (T.K. Wright) (i) I.C.I. have a temperature-pressure test to detect materials which may deflagrate; it measures the temperature and pressure at which high rate decomposition occurs. This pressure must be imposed to prevent evaporative heat losses dissipating the heat of decomposition thus supporting deflagration. (ii) Materials listed by Dr. Grewer deflagrate at atmospheric pressure, presumably because they decompose before volatilisation. (iii) Other materials like dinitrotoluene can be made to show high rate decomposition/deflagration by imposing a nitrogen pressure. (iv) The other important criterion is a pressure-rise time (ca 200 - 400 lb/in<sup>2</sup>) of less than 50 ms.

R/A Agreed and acknowledged contribution.

Q/C (N.F. Scilly) Some organic materials in nitric acid capable of self-sustaining deflagration. Some of these mixtures are detonable --- e.g. the final nitration stage in T.N.T. in which at least one incident has occurred.

- Q/C (R.L. Rogers) Also commented on the risk of deflagration during nitrations and asked what is the cause?
- R/A If you put textile material into the nitration mixture it will ignite and we think this was the cause of ignition because you don't get deflagration in nitration reactions. There is no thermal instability at 80°C. There may be some nitration mixtures which can deflagrate but they contain substances with more than one nitro group.

Paper No.2: Clancey

- Q/C (N. Gibson) (i) Results in Fig.1 were measured at 169°C "A few degrees below decomposition temperature" but table 5 shows decomposition occurring at 70 or 80°C — why?
- R/A That is the runaway temperature for a stored material - temperature outside, whilst temperature inside Dewar test vessel is rising rapidly. For gas evolution measurements we worked at a temperature sufficient to take gas off quickly
- Q/C (N. Gibson) Can you explain difference between two sets of samples, shown in Fig.1 (A,E : B,C)?
- R/A B,C must have contained a contaminant that triggered decomposition of the rest.
- Q/C (P. Charlesworth) On behalf of the manufacturer who submitted written comments (see below), supported the author in presenting a fair assesment of a controversial topic.

Written Comments (J.A. Wejtowicz, Olin Corporation, U.S.A.)

INTRODUCTION

This is in response to the title paper By V.J. Clancey, Presented at a symposium on Hazards From Pressure at the U. of Manchester on June 16, 1987. The title is misleading in view of the author's own conclusions that:

- 1) Calcium Hypochlorite is a reasonably stable material.
- 2) Observed incidences of apparently spontaneous explosions and fires are rare events.

- 3) Many of these incidences have been due to contamination.

Clancey proposes that those unusual incidences not caused by contamination, are due to impurities or by-products, i.e. the rogue drum theory. However, his examples (magnesium, iron, chlorate, bromine, organic matter and chlorine monoxide) are merely speculations that are not supported by facts as the following discussion will show.

Much of the material in his article is a rehash of previous articles (1975-78) on the same subject. Papers such as Mr. Clancey's have been presented over the past few years, with the apparent purpose of discouraging usage of Calcium Hypochlorite and of encouraging restrictions of its use.

The references to bleaching powder are not germane to a discussion of high assay Calcium Hypochlorite. Bleaching powder is not a purified product - it is a mixture of double salts having a low assay of -35% and a significantly lower stability than high assay calcium hypochlorite.

DISCUSSION

Product Safety - Although Calcium Hypochlorite is a strong oxidizer, it is a safe material when stored and used properly. Indeed Clancey himself states that "Practical experiences over many years and involving large quantities has shown that normally the packaged material may be safely stored even under the highest ambient temperatures usually experienced." Calcium Hypochlorite does not explode spontaneously when stored under ambient conditions. It must be contaminated by reactive materials such as oil, grease, debris or other incompatible products such as chloroisocyanurates (TCCA or SDCC), for exothermic or explosive decomposition to occur. Calcium Hypochlorite is not sensitive to shock or friction.

Product Manufacture - Calcium Hypochlorite is produced in modern plants from high purity hydrated lime, caustic and chlorine. Considerable attention is paid to product uniformity, the objective being the production of quality

product for optimal shelf-life and efficacy in use. The product is packaged in corrosion-resistant drums to extend package life and to prevent contamination during shipping and storage.

Product Composition - Commercial 65% Calcium Hypochlorite has a well-defined composition. The main inert ingredient is sodium chloride, with smaller amounts of calcium chloride calcium chlorate, calcium hydroxide, calcium carbonate and hydrate water. Clancey points out that water of hydration desensitizes the product to certain contaminants, and moderates decomposition when the product is engulfed by a fire of external origin. Small amounts of other trace and for the most part inert inorganic impurities from the lime source can also be present. Some of these impurities are removed during processing. Bromine is an unlikely impurity in significant amounts because of the high purity caustic employed as a raw material.

Product Decomposition - The decomposition mechanism of Calcium Hypochlorite is well understood, the normal products are calcium chloride, calcium chlorate, and oxygen. Chlorine is only formed after extensive decomposition has occurred. Chlorine monoxide has never been observed, even in small concentrations, not to mention the 20% necessary for explosion to occur. Therefore, chlorine monoxide is not a likely cause of reported spontaneous explosions of Calcium Hypochlorite. Calcium chlorate has no significant effect on the decomposition rate, as shown by laboratory studies in which it was deliberately added. It is very stable, decomposing only at temperatures in excess of 300 °C. Because of the low concentration of carbon dioxide in air, it exerts an insignificant effect on decomposition of Calcium Hypochlorite stored in a sealed container. The overall effect of carbon dioxide absorption is formation of calcium carbonate by reaction with calcium hydroxide. The trace metal magnesium is present primarily as the hydroxide - an innocuous impurity; and chlorination that

might occur would convert it to tri - or dibasic magnesium hypochlorite - extremely stable compounds which decompose (endothermically) only above 300°C. The iron impurity in

Calcium Hypochlorite is present largely in inert form. Indeed, there is no significant correlation of available chlorine loss during storage with iron content of the product. Because lime-stone is calcined at over 1000°C organic impurities are either oxidized or volatilized and are not present as contaminants in the hydrated lime used for manufacture of Calcium Hypochlorite.

Calcium Hypochlorite is heated to about 80°C during drying and thus is stable at temperatures encountered in transportation, storage and use. Indeed, storage of a 100lb drum of 65% Calcium Hypochlorite at 50°C showed no evidence of self-heating over a 30 day period. It must be borne in mind that product in transit or storage never truly reaches the maximum environmental temperatures because of diurnal variation, and the fact that heat transfer is a function of container size, time, temperature differential between the drum and the air, as well as air turbulence. It is common practice to store product in ventilated warehouses to reduce temperature exposure and prolong shelf-life.

- Q/C (C.R. Jones) Following your study what recommendations would you make for safe storage?
- R/A Difficult advice to give. Reliable manufacturers give very good guidance: particularly to avoid contamination once opened; store minimum amount; site storage for minimum damage in event of explosion. Incidents are rare but a current enquiry relates to an explosion which killed two men --- treat it with care.
- Q/C (B.J. Tyler) Is a drum within a stack of drums more likely to behave, when self-heating, as a single drum (due to convection) or as part of a larger mass equivalent to the combined contents of the stack?

- R/A The significant radius (in the Frank -Kamenetski equa., Ref 9) is something like half the side of the cube (see Bowes, Ref. 10). With close stacked rectangular packs one is very close to the total size of the store but with cylindrical drums convection will occur, some intermediate situation applies --- depending upon how closely stacked.
- Q/C (N. Gibson) You referred to the I M D G Code. What recommendations were made?
- R/A Only that this substance was entered in the Code as dangerous, requiring special handling.
- Q/C (B.J. Thomson) Asked for views on Ca hypochlorite detonation being initiated. Lieber (of B.I.C.T., Bonn, W. Germany) got detonation in steel tubes at 1000 m/s using a booster pellet; this seems a low speed for detonation however.
- R/A (H.Klusacek) Lieber has shown also that other substances (eg. potassium chlorate, sodium nitrate) can propagate a "low velocity detonation" by using T.N.T. as a booster. So far the results have no practical meaning for handling or storing the substances.
- Q/C Can you make any further general recommendations for storing hypochlorite.
- R/A
- (i) Risk is worse when close packed
  - (ii) Use a reliable manufacturer.
  - (iii) Store as little as possible.
  - (iv) Keep in a place where damage would not be serious.
  - (v) Do not store for long period.
  - (vi) Ensure drums do not have plastic liners.
  - (vii) Material with 7/8 % water is more stable.

Paper No. 3 : Klais

- Q/C (G.A. Whyte) (i) Questioned what happens when stirrer stopped and catalyst settles. (ii) How significant is new catalyst?
- R/A (i) There is no self-accelerating heating at temperatures below 40 - 50°C. (ii) New catalyst is certainly more dangerous but it is very important to consider the whole mass of catalyst in the system.

- Q/C (N. Gibson) Boiling off of methanol would be significant at lower pressures.
- R/A Only dangerous at pressures of the order of 200 bar. Maximum temperature is controlled by the partial pressure of methanol.
- Q/C (N. Gibson) If you had been testing a new process for safety, could you have predicted what would happen in the event of stirrer failure.
- R/A Could not predict the methane formation but total hydrogen absorption is a measure of the potential for methane formation and also a limit
- Q/C (J. Steinbach) Did you observe any differences between experiments with and without the presence of substituted acetonitrile?
- R/A We did both experiments; starting without the stirrer did not change the situation. A similar result was obtained in the presence of reactant.

Paper 4 : Bond

- Q/C (O. Klais) Example 1, of unexpected decomposition of hydrazide is a warning against taking measures only against dust explosions --- ignoring hazard of exothermic decompositions of the bulk material. If the fill ratio had been greater the potential pressure rise would have been much more than 10 bar.
- R/A Stressed importance of foreseeing all possible deviations that could create a hazard, backed by literature search as followed the first reported case study. Here the ethylene cracker side stream contained about 300 p.p.m. of acetylene which was not taken into account. Note the importance of getting all such information into the literature.
- Q/C (H. Klusaek) Was there any proof of formation of trisethanolamine iron (example 2) on the coil. On storing monoethanolamine with iron powder at 70°C, we found no such compound or any unstable substances.

R/A This came from an old record (no further information available) but the temperatures of formation and decomposition of the iron complex were taken into consideration and no other explanation could be found.

Q/C (K. Palmer) Referring to example 3, the design of an explosion venting system should be based on the maximum decomposition as well as dust explosion.

R/A Plant was probably designed for a different product and this decomposition causing a large volume increase was not realised

Q/C (N. Gibson) Is there any test to determine risk of ignition due to friction?

R/A No — and in this case identification of the cause was partly supposition, but we found it could be made to go by rubbing the surfaces together.

Paper 5 : Tyler

Q/C (R.L. Rogers) Can you explain the absence of a small temperature rise at plate temperatures slightly below ignition temperature as observed with other systems and predicted by theory?

R/A In the cube test you get 20-30°C rise in centre of cube just before ignition — regularly, seen. In cube with non-reacting system there is a uniform temperature distribution. On the plate there is a difference between the temperature profile shown and a straight line distribution so we do see the difference between reactive and inert materials (reference to experimental curves).

Q/C In the cube test you do get a temperature rise above the uniform value.

R/A We did not see this with pure dithionite but when diluted we saw temperature rising above plate temperature.

Q/C (T. Grever) Sodium dithionite gives two exothermic effects:

- (1) decomposition of the salt
- (2) self-ignition of the products (sulphur).

Because your results are influenced by this two-stage process they cannot be generalised.

R/A The kinetics were measured under the same conditions (in air) as those on the hotplate and therefore appropriate. What matters is whether we have a describable rate of heat release — to feed into the model to show whether the bulk material will ignite. Do we have an appropriate model for the heat release of material as in the lab? We found (by accident) that if products of 1st. heat release are kept on the plate at 250-300°C after an hour a further exothermic decomposition of the products occurs.

If material is put on to the plate at high temperature (350-400°C) reaction occurs and if the temperature is taken down 200°C another temperature limit is found. When carrying out high temperature experiments the low temperature exotherm takes place whilst the layer is built up (10-30s) so is not seen — only the ignition characteristics of the second exotherm are seen.

Q/C (J.H. Burgoyne) Your last slide, not in the paper shows a procedure for establishing the initial self-heating temperature for dust layers of greater thicknesses. Could we record this please?

R/A Yes, I will set out the procedure

NOTE The following was submitted after the meeting:

Obtaining Ignition Temperatures for Layers

1. Use depths of  $\geq 20$ mm.
2. Measure  $T_{ig}$  for two or more depths.
3. Estimate E from standard plot using constant  $d_c$ . Use this to calculate values.
4. Estimate  $\alpha$  values (e.g. from T profiles at steady state after non-ignition). Use Thomas & Bowes data to allow for change of  $d_c$  with  $\alpha$ .
5. Return to step 3 and use variable  $d_c$  to get new E value; iterate to constant E and plot a graph.

6. Use this graph to extrapolate to get T at other layer depths.

Q/C (N. Gibson) How is the last slide applicable to decomposition with gas evolution as most solids do — you chose a test material that did not?

R/A If the Frank-Kamenetski method is applicable then this method is also. When oxygen is required for combustion there is counter-diffusion — not important in development stage, but in ignition stage. We did some work which showed that the ignition started at the top and burnt downwards.

Paper No. 6 : Gibson

Q/C (Chairman: J.H. Burgoyne) Paper will be a source of reference for a long time — reflecting a large amount of experience.

Q/C. (Th. Grever) Scheme presented is in good agreement with that produced in Germany. I suggest adding:

- (1) limiting values of reaction and decomposition energies which decide whether a reaction is hazardous or not
- (11) rules for the safe handling of batch and semi-batch reactions related to reaction time, cooling capacity, etc.

R/A We feel that rules have to be over-safe to cover all cases and better to study each case separately working through the system outlined in the paper.

Q/C. (H.A. Duxbury)

- (i) You have emphasised the importance of specifying the minimum runaway temperature. Some processes normally operate at such a temperature and are controlled by cooling. Hence the need for 'Hazop Studies' to identify all possible causes of cooling failure.

- (ii) You showed an example of a reactor with the top blown off because the reaction had become violent by the time the failure pressure was reached. Sometimes a smaller vent which operates at a pressure sufficiently below the maximum safe pressure will prevent the reaction from becoming violent.

R/A You have to think in terms of reliability since process control relies upon reliability of measuring the right temperature (Level 4) and acting accordingly. This study precedes Hazop then go on to assess reliability.

Q/C (B.J. Tyler) Can you give examples of inherently safe approaches to batch reactor operation?

R/A Generally a matter of reducing the potential for hazard — e.g.

- (1) if all reactant goes in at start, agitator failure can be very hazardous, but if feed is continuous or gradual it can be cut off if agitator fails,
- (ii) reduction of batch size and compensating in other ways.

Q/C (J. Bond) A very useful paper but do you have any similar procedures for trace chemicals?

R/A Not personally involved with toxics but I.C.I. has a set of procedures. (Chairman: no doubt information could be made available).

Q/C (D. Klais) To operate safely the minimum temperature at which uncontrollable chemical reaction starts is needed. Can you give guidance how to determine this temperature without the complications of heat transfer information, etc?

R/A You must simulate the process in terms of heat loss, time — temperature profile and look for any induction periods. He expressed concern that you have no control over the information going into the computer bearing in mind: "rubbish in — rubbish out".

Q/C (H.A. Duxbury) You don't just have to simulate the NORMAL process, but all possible variations.

R/A Yes, there is an unending test situation. So you put in process control and limit the variation.

Q/C It is necessary to study normal conditions anyway.

R/A Find out what the plant operator says about divergence from normal operation (e.g. plus-minus temperature variations and test accordingly).

Paper 7: Wright

Q/C (K.F. Ryan)

(i) Would you please give an order of magnitude of the costs

(ii) You have a sophisticated system for pre-assessment — what about plant problems

R/A (i) Equipment was designed in-house.

Rough costs: £8000/9000 plus ancillary equipment including gas evolution measurement somewhat more, plus micro-computer £1000/1500;

(ii) We would prefer to simulate the reaction even if given a plant problem.

Q/C (J. Steinbach) Heat flow calorimetry is a very powerful tool in hazard assessment. However, your technique is such that you keep heat transfer area constant and small. Consider what happens with a semi-batch process, initial batch volume exceeding heat transfer area, and a temperature at which reaction is slow. One assumes that the reaction will proceed without any dangerous accumulation of added reactant. In practice you have a larger heat transfer area initially so the reaction will proceed more slowly than in the experiment and could lead to a dangerous accumulation of reactant. How do you take care of this problem? (Ref: Chem. Eng. Sci. 41,4, 1081-1087, 1986).

R/A Referring to Figure 1 — as the volume increases the H.T. area does not; the H.T. coefficient is about 250W/m<sup>2</sup>K, similar to that in a chemical reactor.

NOTE There seemed to be some misunderstanding of the question and chairman asked for discussion outside the meeting.

Paper 8: Craven

Q/C (O. Klais)

(i) When the heats of formation of the decomposing material and the products are large compared with the difference between them, it is doubtful whether the accuracy of the method is sufficient to discount the possibility of a runaway.

(ii) The technique also depends on assumption of total reaction products, ignoring side reactions hence is limited to the worst case of decomposition into stable products with low heat of formation.

R/A (i) The method does not specify that there will be trouble but indicates (in the case of a small change) that there could be a risk.

(ii) I chose average bond energy values (Sanderson) which tend to overestimate heats of combustion and decomposition — hence safe values.

Q/C Interpretation difficult if values are small.

R/A Exothermicity can be estimated in this way but would not argue about interpretation though there is no doubt about comparison between say 1000 and 200 cal/g.

Q/C (J. Steinbach) Referred to studies on 30 organic compound to test the CHETAH ASTM program. Your results are often closer to experimental. Difficulty is found with substituted aromatics — is there any further data on (say) difference between ortho and para substituted compounds.

R/A Stressed the value of Sanderson's work, stating that two more volumes are now available — the third including new data on covalent bonds but have no specific



information on your query.

Q/C (Th. Grewer) What is the difference between your method and the older methods of van Kleberma and Uchida?

R/A No difference in principle but the data of Sanderson has produced better results.

Q/C (N.F. Scilly)

(i) With a compound like an amide there is neither a true carbonyl nor single C-N bond because of enolisation. By "swings and roundabouts" the method will probably average it out.

(ii) Your structure for T.N.T. (page 101) is of a nitrate not a C-NO<sub>2</sub> compound.

R/A Re (ii) it depends which book you use! If one studies the method of preparation, it seems that there's little difference in energy between the two (probably tautomeric) forms and we do not have bond energies for the nitro form.

Video Training Package on Inherently Safer Plants (T.A.Kletz)

The video presented to the meeting after Paper No.8 by Professor Kletz explains the principles of a radical and yet fundamental approach to the design of safer process plants. Inherently safer design proposes that hazards should be removed early in the design stage.

The video is available from The Institution of Chemical Engineers, Rugby.

Paper 9: Bourne

Q/C (J.H. Burgoyne) Clarification of several points:

- (i) Where will papers be published?
- (ii) What will be the scope in relation to this presentation
- (iii) Can you give references to the Russian work?

R/A (i) Chem. Eng. Sci. (2 papers 1987)  
 (ii) Physical and heat transfer rather than

reactor safety; Combustion, Explosion, Shock Waves. Merzhanov 1971 (2 papers)

Note: Russians did not work in the turbulent region.

Q/C (R.L. Rogers)

(i) What was the temperature in the vapour phase and how did it vary?

(ii) Would you amplify the reason, for the difference between the small scale and the 400 l work?

R/A Sometimes the traverse was carried above the liquid surface into the stationary air (or nitrogen) space. The temperature fell ten~~s~~ of degrees within a few mm.

(ii) There many quantities that determine the degree of vertical stratification: thermal conductivity of fluid, volumetric coefficient of expansion, kinematic viscosity — also the amount of cooling surface per unit volume.

That is why the term was in the modified Rayleigh No. Since we are dealing with transfer to jacket (not coil) the surface/unit volume decreases with scale. This is why thermal stratification in degrees in the large vessel was 10x that in the small vessel.

Q/C (G.A. Whyte) Has any work been done to compare glass-lined vessels with unlined vessels?

R/A I only know of internal work at Ciba-Geigy — not accessible. We have been dealing the coefficient for the fluid in the reactor. Overall heat transfer calculations must take into account also any dirt coefficient, glass lining, wall etc for whatever type of reactor is used.

Q/C (J. Steinbach) How did you carry out the active experiments involving addition of catalyst without causing agitation?

R/A The trimethylphosphite was in the vessel, heated to 50°C with nitrogen gas agitation to ensure a uniform temperature; then the catalyst was added and mixed in (less than 1 minute) before the gas stream was stopped. Uniform dispersion and temperature were assumed.

Paper 10; Cronin

- Q/C (H.A. Duxbury) Some points for clarification:
- (i) Can you use the equipment for high reaction rates/runaway?
  - (ii) At what pressure can the power compensation Dewar operate and is it of glass?
  - (iii) What is the heat capacity and what ratio to the contents?
- R/A
- (i) At present working in open laboratory but could modify for use in explosion cubicle.
  - (ii) atmospheric at present, it is glass. We hope to extend the range of temperature and pressure operation
  - (iii) about 300J/K, that is about 15% of contents when water. We measure heat capacity before and after and take into account. With fast reactions there can be a problem of superheating of the mass.
- Q/C (J. Singh) All the adiabatic equipment tested had thermal capacity factors ( $\phi$ ) of 2-3½ and yours was greater. This will involve considerable extrapolation of kinetic rate when used to the full temperature range.
- R/A In decomposition reactions studies we stick rigidly to initial rate kinetics (first 5% conversion) — hence extrapolate downwards.
- Q/C This is valid for storage conditions but not for extrapolation upwards relevant to runaways
- R/A Agreed one has to be careful.
- Q/C (Th. Grever) Why do you think a temperature increase of 25K is hazardous?
- R/A This is a safety margin for storage.
- Q/C It is rather low.
- R/A These margins are somewhat arbitrary — if not possible to operate a process within such margins, it would have to be increased. Or with close process control the margin

might be decreased. The limit of heating may well be the temperature of the heating medium under fault conditions.

- Q/C (O. Klais) Why do you need larger scale tests, not trusting the results from small scale tests.
- R/A We had some materials which were problematic where temperatures depended on test method particularly testing butyl peroxybenzoate (page 116). At 60°C heat generation 0.03W/kg is an order magnitude lower than can be detected by sensitive small scale tests so recommend heat accumulation storage as back-up. With many materials to examine, use the small scale at first (time, cost, hazard of large scale). By calculating activation energy and extrapolating downwards we got 55-60°C in agreement and manufacturer's recommendation.
- The thinking behind the GADT test is that it gives heat less characteristics representative of commercial packages and with only 5000g mass there is a Dewar within an oven.
- Q/C He questioned the accuracy of data for storage vessel doubting assumptions about heat losses.
- R/A Referred to temperature gradients within the mass and resulting uncertainties.
- Q/C (H.A. Duxbury) Asked about a testing service at South Bank Polytechnic.
- R/A This service will officially open on 15th. July.
- Q/C (P. Rutledge) In Table 2 page 117 the value 144.1 should read 1441. (Agreed by author).
- Paper 11: Margetts
- Q/C (O. Klais) Acknowledged that safety and reliability of production can be increased by a P.L.C. But is one P.L.C. sufficiently reliable to guarantee that trip system will always work — e.g. at beginning of a runaway reaction?
- R/A Hazard study should include the programmable device. Suppose we have one failure per year due to unforeseen occurrences. Since we can test between each batch the

chance of failure during the batch time process is low. If it is essential to operate the trip one can increase reliability by installing two devices, ideally of different types programmed by different people. Alternatively rely on P.L.C. mostly but also have a bursting disc.

Q/C (N.F. Scilly)

(i) Two programmers from the same company could make the same error — a rather subtle common mode of failure. It's better that they come from different sources.

(ii) Is it vital for the program designer to be in the final H A Z O P.

R/A One way is for the client to supply one programmer and the supplier the other.

Q/C (R. Duffield) Would the best way of ensuring safety be to use hard wired interlocks as back-up for catastrophic failure modes and P.L.C. only when failure is "inconvenient".

R/A Yes, many companies are doing this but some may accept the use of two independent P.L.C.'s as mentioned earlier. Remember each hard wired system has to be designed, installed and regularly tested.

Q/C (E.W. Hutchinson) One fault at a time is simulated to determine its effect. In practice multiple inputs can occur leading to processor "hang-ups". Only a process simulation, possibly requiring a computer (which also requires Q.A.) can overcome this.

R/A This highlights the problem of bringing-in another computer to test a computer. With batch reactors, generally few in number the problem is not so great and can be dealt with by checking every input and response of every output and checking likely disturbances. In a complex situation (say, a nuclear plant) the problem is very large.

Q/C (G.A. Whyte) How would you recommend an acceptable approach to operators who are to be involved with P.L.C.

R/A Generally operators are receptive to the system. They become monitors of the process stages, checking and taking action if a fault develops. Operators have to be well-trained and able to visualize what happens on the plant from what they see on V.D.U. They must be involved in equipment and testing procedures.

Q/C (J. Munnings) Do you propose that HAZOP on the control system be carried out with normal process HAZOP or separately. The latter may be more practical but may highlight potential problems too late.

R/A This is dictated by the project time scale. It is usually necessary to define and order process equipment before there is time to study and define the control philosophy in full detail. So in practice this HAZOP study is done later.

Q/C (P.F. Nolan) Is it vital for the program designer to sit in on the final HAZOP?

R/A Yes, definitely! Problem is often that program writing is put out to separate contract making it difficult to achieve.

Q/C. (C.A. Griffiths) The application of P.L.C.'s to control hazardous reactions does not necessarily reduce the capital cost. Sometimes the result of a mini-HAZOP on process control is increased instrumentation and installation costs — particularly in a hazardous area requiring expensive electrical protective equipment. (Comments based on experience in converting a manually-controlled plant).

R/A Yes, in some areas low voltage supplies are needed with precautions against high voltage break through.

SESSION 3 VESSEL PRESSURE RELIEF

(Chairman: A.J. Margetts)

Paper No.12: Fauske

Q/C (H.A. Duxbury) Is the factor of  $\frac{1}{2}$  in equation 1 and Fig.3 theoretical, empirical or an approximation.

- R/A It is an approximation based on the average of  $dT/dt$  at the set pressure and at the maximum (when  $dT/dt = 0$ ).
- Q/C (P.R. Norris) How does one determine the parameter  $\alpha_D$ , the turnaround freeboard volume?
- R/A (i) can be determined in the VSP apparatus;  
(ii) Otherwise can be set equal to 1.0  
--- assuming homogeneous venting.  
This is safe.
- Q/C (L. Friedel)
- (i) You demonstrated good agreement between predicted and measured results. Which parameters did you measure?
- (ii) Having calculated the required vent area, how do you calculate the predicted mass flow rate when critical flow is established?
- R/A (i) We measured  $\Delta T$ ,  $\alpha_D$  and  $(dT/dt)$ , as indicated Fig. 3.  
(ii) No need to calculate the mass flow rate which is incorporated in the equation for "A" (Fig. 3). This fits the measured data.
- NOTE Question (i) may not have been understood.
- Q/C (J. Munnings) How applicable is the equation For non-reactive systems when a fire heats the bottom as well as the sides of a vessel?
- R/A Tests have shown that, because of strong circulation effects, boiling is confined to the boundary layer at the wall.
- Q/C Having calculated the vent area, what mass flow should be used for sizing the downstream dispersion system?
- R/A Use the expression for "W" given in Fig. 3.

WRITTEN CONTRIBUTION (M. Ottaway, Colombia Scientific Industries)

Dr. Fauske, during your talk you showed a diagram contrasting VSP data with ARC data.=

This data has been shown on many occasions and I have refrained from comment and allowed you your 'dig' at the ARC. Today, however many people have asked me to respond. Before doing so can I say that much of my response is detailed in CSI's technical information Bulletins; Archives 7 and Archives 8. In the past I have hesitated to respond partly because I consider that to compare two techniques using one 'anonymous' sample is petty and partly because the comparison was presented in a somewhat cavalier manner for the effect, primarily to aim to 'show that the VSP is better than the ARC'! but my comments may be summarised.

Firstly, the ARC data was shown for a test at  $\phi = 2$ . This is an arbitrary figure and is higher than normally used in ARC tests. Indeed dependent upon sample and bomb type used it is possible to use the ARC with  $\phi = 1.1$  or even lower.

A more major point however, is that you show the data from a self-heat rate of  $1^\circ\text{C}/\text{min}$ . You have chosen not to show all the data and this is misleading. The VSP will detect an onset from  $0.2^\circ\text{C}/\text{min}$  and the ARC at 10 times greater sensitivity at  $0.02^\circ\text{C}/\text{min}$ . Thus you have omitted data from your illustration. Arguably this is the most important data — it is the initial low temperature self heating information. Now if the data was extrapolated (assuming Arrhenius kinetics) you will see that the VSP will detect onset near  $20^\circ\text{C}$ ; the ARC ( even with  $\phi = 2$ ) will show onset near  $0^\circ\text{C}$ . The reality in this comparison is quite the opposite of your portrayal!

In addition you state and emphasise that "the ARC shows 1 exotherm, the VSP shows 3". How can you substantiate this?

Again your illustration is misleading; in that it emphasises the data recorded at very fast self-heat rates. Most of the VSP data was recorded at rates above 50°C/min (to a maximum rate of 1500°C/min). Thus the vast majority of your data has been recorded within a time frame of 60 seconds. I suggest that such information has little relevance if it is reliable. Adiabatic calorimetry relies upon good operational adiabaticity and thermal equilibrium within the sample to yield reliable self-heat rate data.

It is unfortunate that you are willing to show information from a sample which you will not name and because you are using this to compare two techniques I suggest this is a particularly unscientific exercise.

However there is another aspect which is worthy of more general discussion and does not emerge from this data. This afternoon a lot has been said about the  $\phi$  value of adiabatic calorimeters. Perhaps it should be added that there are two areas where deviation from adiabaticity occurs during experimentation with an adiabatic calorimeter or Dewar apparatus. There is heat lost into the sample container ( $\phi$ ) and there is heat lost from the container (operational adiabaticity). Both should be known and corrections made. The  $\phi$  value is a relatively simple correction and is easily and usually applied.

Correction of loss of heat due to deviations caused by poor operational adiabaticity are often overlooked — and are thus most important in any discussion on techniques. In the ARC the environment surrounding the sample bomb is controlled in three separate zones; the bomb to calorimeter temperature differences are controlled to 0.01°C. The differences are continually monitored in the ARC and a correction may be made but is usually too small to be of any significance.

Within the VSP, there is just 1 zone of control and it has been reported (Noronha, Int' Loss Prevention

Symposium, Cannes 1986) that a 5°C temperature difference exists. Therefore there are two aspects to consider in contrasting the ARC and VSP comparative data presented. Firstly, on analysis of the data to consider its meaning and relevance and secondly to consider the reliability of the data produced from an understanding of the limitations of the technique employed.

R/A ARC was developed to detect the onset of instability and is very good for that. Unfortunately it has been used for obtaining data for vent sizing. But the data requires correction. This can be done for first order reactions if you have the kinetic data but is very difficult or impossible to do this for other cases. The VSP apparatus is fully adiabatic so that vent sizing data can be used directly. In extreme cases the two methods can give vent sizes differing by 10x.

NOTE Chairman suggested continuing discussion outside the meeting.

Q/C (R.L. Rogers) The concept of adiabaticity was covered at a previous symposium (Hazards IX). There is no problem with the Dewar. One must generally use a technique suitable for the data required.

R/A Agreed with this.

Q/C (M.C. Jones)

- (i) What is the minimum freeboard space needed to guarantee one phase flow, from a heated non-reacting system?
- (ii) What happens to a liquid stored under pressure and heated when the relief valve opens so that the liquid becomes superheated?

R/A (i) The advice given in the paper applies to vessels that are full and non-foaming (see page 138). Further advice is also given for foaming liquids.

(ii) For a pressure vessel, size the rest for vapour-only flow. If owing to oversizing of the vent, two phase flow is initiated, the vent will still be safe.

Q/C (J. McQuaid) What rate of temperature rise can the VSP apparatus reliably record?

R/A It will, reliably record very high rates — as high as anything that is relevant to design of relief system.

R/A In response to questions about assuming one or two phase flow Dr. Fauske recommended always using one phase flow, for venting under external fire conditions. Miss Wilday had recommended using two phase flow for vaporisers because the rate of heating was much greater.

Q/C (R.C. Gray) Your comments on liquid swell at atmospheric pressure differ from Forrest's (DIERS) work predicting at least 10% for non-reactive liquids at their saturation temperature (fire engulfment of storage tanks, relief set pressure up to 5 psig). Is the limited experimental data (Fig. 6) accepted by DIERS in support of void fraction values and side wall heat input as from recommendations for non-reactive liquids under such conditions?

R/A Forrest's paper was based on theoretical work and gave safe answers. Subsequent experimental work has shown that, vapour venting only for non-foaming systems is safe — even if vessel is full.

Paper No.13: Klein

Q/C (N. Gibson) In a batch reactor one reactant may be a reasonably well distributed powder (say) 1-2 times liquid density. On vent opening powder will be entrained. Can you model this flow and can the DIERS equation deal with it?

R/A No experience of modelling this condition. Provided the solid dispersion is a homogenous fluid you can use the model.

Q/C Does it depend on density difference — thinking of polyethylene or polypropylene granules?

R/A You could use a drag coefficient based on the size and shape of the particles.

Q/C (H.A. Duxbury) Can your model handle two liquid phases plus gas?

R/A Yes, quite possible.

Q/C (G. Whyte) Are flame arresters taken into consideration?

R/A No we have not included them but you could consider them as a restriction in the flow.

Q/C (L. Friedel)

(i) Is the initial depressurisation rate immediately on vent opening isentropic vapour expansion?

(ii) When does the flow become homogeneous two phase?

R/A (i) I would say mostly isentropic expansion.

(ii) For the model we do not specify that flow is homogeneous. There is drag between gas and liquid which gives it a disengagement which depends on the void fraction and the model takes care of that.

Q/C (H.A. Duxbury) This is some misunderstanding about your reference to detonation. Can you relieve detonation?

- R/A NO. I was referring to prevention of the run-up to detonation.
- Q/C (G.A. Whyte) Does the system take account of temperature variation?
- R/A We do have temperature variation along the axis of the vessel.
- Q/C What about thermally insulated vessels?
- R/A Yes that is possible with the model.
- Q/C (F. McKeevor) I question the applicability of the model where the assumptions may be inadequately founded. For example how robust is the model for multicomponent mixtures if vapour-liquid equilibrium data is only for two?
- R/A A problem for any model. We have our own vap.-liq. equilibrium models built into the program and it needs the data for each of the components.
- Q/C (H.A. Duxbury) In what form is the JAYCOR information available?
- R/A Versions are available for main computers and also for a personal computer. I can give you all the information and provide a demonstration.

Paper No. 14: Maddison

- Q/C (H.A. Duxbury) Referred to typical curves for vent size against over pressure (Figs. 10, 11, page 173) on inaccuracy of the method. But even if the method was exact, you would still get that shape — it is general.
- R/A Yes agreed. This point is brought out in the paper. He stressed that the same data is needed whether you use Leung's method or the simpler formula mentioned by Fauske.
- Q/C (L. Friedel) Some reacting systems foam a bit and others much less. What is the limiting value between these extremes for hydraulic design purposes.
- R/A It depends on the materials being used and especially on impurities present. We would generally assume homogeneous behaviour and if this led to a very large

- vent, look for operating experience to show whether to expect foaming. Generally we do not expect foaming.
- Q/C (H.A. Duxbury) From examined cases, foaming was rare compared with two phase flow.
- Q/C (K. Ryan) One should not only consider the effect of discharge piping on the vent sizing but also any restriction between the process and pressure relief valve (e.g. a bursting disc used in combination with a valve).
- R/A Stressed that flow through the whole relief system must be considered. Sometimes condensates/deposits on the process side can also be a problem.
- Q/A (J. Singh) Concern about the phi factor — it is more certain in the Fauske method than the I.C.I. — reasons given. Is it not better to have a low phi?
- R/A There is a lot of metal on top of the Dewar. Note that tests are taken into consideration as well. In the case of runaway reactions the temperature change is so rapid that the phi factor value does not really matter; it depends on the induction time
- Q/C (H.A. Duxbury) In the paper you quote rather high values (phi) — equipment can be as high as 1.27.
- R/A This depends how far we fill the Dewar whilst allowing for expansion; at 70-75% fill phi is typically 1.05 to 1.11.

Paper 15: Duxbury and Wilday

- Q/C (N. Maddison) The value of  $q$  in Leung's equation referred to in the paper is actually  $\bar{q}$  — the arithmetic mean heat release at disc rupture and allowable over pressure.
- R/A Agreed — if not stated in our paper, we give full references and recommend using them for fast detail. This is the main reason why the method oversizes with high overpressures.
- Q/C (R.L. Rogers) Could give some indication of the difference in vent diameter calculated by different methods for the same system?

- R/A (i) Difference between methods not as important as ensuring that all factors (e.g. long vent lines) are allowed for.
- (ii) Make sure you choose a valid method rather than the best one.
- (iii) Ease of use — for example Leung's method for vapour pressure systems because it is easy and quick. Different methods should give vent sizes within a factor of 2.
- (iv) Before DIERS we would use both Boyle and modified Boyle (given in Ref.1) taking the smallest size since both are safe. SIZES from DIERS methods don't differ very much and it is more a matter of convenience in the particular circumstances.

Q/C (P.R. Norris) In the past large safety factors were applied. Have improved methods changed I.C.I. attitude on these.

R/A We used to use a factor of 2-3 on AREA from the literature. Now there may be differences of opinion. Firstly, it depends on the data (use worst case). Secondly, the accuracy of the method must be considered. If we calculate flow rate using HTFS methods, official and comparison data shows them to require a factor of 2 for two-phase flow in long lines with friction. But for short lines we accept factors as low as 1.2 — on absolute minimum since Fanning friction factors are no better than  $\pm 20\%$ . We need a safe size, not the best estimate.

Q/C (J. Singh) Can you comment on the use of the equation for G (page 179) when you know dp/dt to gassy systems.

R/A The equation is for vapour pressure systems. A different form of it can be used for hybrid systems. There are methods for gassy systems given in our references. We have tried to restrict the paper to publicly available references (rather than the DIERS report). The DIERS method for gassy systems is available and easy to use. (Corroborated by H. Fauske).

Q/C (K. Palmer) Some propane bottles are fitted with spring-loaded relief valves to relieve overpressure in the case of fire. Discharge may be vapour or liquid depending on whether upright or lying down. Can DIERS methods be used to size the valve.

R/A You could use the individual equations for calculating the flow. (Attention was drawn especially to the equilibrium rate method).

Q/C (H. Fauske) (i) The short form equations are useful for checking. In fact we use the Leung method for our clients work but I personally use the short form to check and if there is more than 20% discrepancy the report is sent back for re-checking.

(ii) The short form equations are also useful for calculating energy release — e.g. when equipment is to be used for different materials than designed for.

(iii) Nomogram is O.K. for long lines up to L/D of 400 but divide by 2 for nozzles.

R/A Would endorse this approach which is consistent with our view. Before we had your equation with the 0.5 factor in it we used the earlier Leung equation (Fauske) With the factor the methods give very good agreement.

Q/C (J.S. Cook) Sizing calculations depend entirely on the accuracy of worst case assumptions. What confidence do you have that the worst case scenarios are correctly selected?

R/A Referred to N. Maddison saying that all papers assume dT/dt is measured. This is convenient but not essential since it can be calculated from heat release rates not based on measuring rate of temperature rise. (N. Maddison: referred to the method given in Paper 7 for measurement of rate of temperature rise).



- Q/C Doubts about identifying the worst case.
- R/A Following the study of the reactions and HAZOP studies does not know of any cases where the worst has been missed. He recognised that some chemical systems are so complex it is difficult to be certain of everything that could go wrong whereas polymerisations are usually relatively simple.

Paper 16: Wilday

- Q/C (N. Maddison) Which of the two DIERS methods did you use to calculate level swell — was it the "volume method".
- R/A Yes, this is appropriate, when gas/vapour is generated in the mass — the other when sparging from the bottom.
- Q/A (A.J. Margetts) In your example 1, what design pressure was adopted?
- R/A The highest one. Method 1 gives same size as method 3 for that design pressure because steam was not restricted. At the design pressure, temperature difference between steam and process fluid small — hence little heat transfer. Method 1 only considers design pressure — gave smallest size so we could go for a smaller more compact design.
- Q/C (J. Singh) Question about pressure rise turnaround by the time only vapour will be discharged. In data for method 3, is the rate determined by vapour flow?
- R/A No. that point is determined by getting enough two phase mixture out before the pressure reaches design plus 10% so that it disengages — larger than required for vapour only.
- Q/C Your example shows that you can reduce vent size by restricting steam supply, etc. What about the external fire situation?
- R/A These vaporisers were to be installed in an area where no flammable materials were used, so no problem.
- Q/C (A.J. Margetts) Drew attention to the Safety in Operations Group of the I.Chem.E; — not confined to members — as secretary he has full information.

Information about DIERS (H.A. Duxbury, J Wilday)

- (1) DIERS USER Group. Joining is free — contact Harold Fisher, Union Carbide corporation, P.O. Box 8361 Bldg. 2000-4125, South Charleston, W.Y 25303 U.S.A. (phone 304-747 4141) or Jill Wilday at I.C.I. Engineering Dept. NORTHWICH, Cheshire.
- (2) DIERS USER Group (U.K. and Europe) Restricted to those using the equipment or methods. Secretary: Jill Wilday (as above).
- (3) DIERS Reports of all research done and SAPHIRE PROGRAM. Available for purchase from A.I.Ch.E. Caution was given, about the earlier reports of a developing research project.

Paper No. 17: Burgoyne

- Q/C (N. Maddison)
- (i) Interceptors are generally large and present an ignition risk if an electrostatically charged mist is formed.
- (ii) High velocities encountered during pressure relief (particularly when carrying particulate material) is a good mechanism for causing charge accumulation in any non-conducting (plastic) valves or other components.
- R/C Stress that this is a problem that can only be looked at in detail in each situation. Avoid non-conducting liners etc. whenever possible in relief systems.
- Q/C (S. Richmond)
- (i) Agreed that this is a difficult area and there is a need for preparation of detailed guidance (say, by I.Chem.E.).

- (ii) There is a working group, within the Inspectorate of Pollution, on "Releases from Safety Devices". It issues guidance notes to inspectors and welcomes any contribution from outside.

R/A Assume you mean principles, not detailed design. Suggest that I.Chem.E. do something to bring all available information together.

Q/C (J. Wilday) Design of separators is a problem for foaming discharges that are inherently surface-active. Methods of API 521 and Grossel's recent papers do not apply — perhaps another area where work is needed.

R/A API was mainly concerned with separation for flares to ensure no large amount of particles going uncombusted. Grossel's paper is more relevant but does not cater for foams. Foam breaking techniques should be considered but it will be difficult to handle relief flows. One hopes it will not be often!

Written Comments submitted subsequent to meeting (J.R. Tippet<sup>s</sup> and G.H. Priestman: Dept of Chem Eng. Sheffield Univ.)

Professor Burgoyne's paper leads to the consideration of methods for reducing the severity of accidental toxic discharges. We describe here three hypothetical applications of non-moving-part fluid-handling technology which might form the bases for practical development, or at least draw attention to new approaches.

As conceived in the paper, we assume a reaction vessel which is protected (for example) by a bursting-disc and emergency discharge line passing through clean-up equipment to a safe dispersal system. The first two suggestions concern dispersal of gaseous effluent. The problem to be overcome is the varying magnitude of the effluent flow pulse. Suppose a stack is designed to cope with the initial peak flow; when the flow diminishes the stack would be oversized leading to insufficient upward momentum and possibly excessive toxicity con-

centrations near to the stack. Essentially the problem is one of satisfactory operation over a wide turn-down range. Possible solutions are indicated in Figs.1 and 2 and described in the following:

#### Vortex Amplifier Relief Stack Switching (Fig.1)

The effluent pulse first enters a vessel which acts in a circuit-sense as a capacitor in a pulse-detecting network. Flow then goes to a small stack and also to special form of vortex flow switch (called a "4-terminal turn-up vortex amplifier" or VA). A second line from the vessel feeds the VA control port. Outputs from the VA go either to the small stack or to a much bigger "relief stack".

For low-intensity discharges, the circuit is adjusted to cause swirling flow in the VA. The flow completely bypasses the reliefstack so that it all discharges through the small stack.

When a high-intensity pulse occurs, the VA switches and opens a low-resistance path to the relief stack. The discharge is then shared by the two stacks. The major flow path is now through the relief stack.

#### Ejector with Non-Linear Entrainment Scheduling (Fig 2)

The effluent is fed to the nozzle of an ejector whose mixing tube and diffuser have been carefully matched to give the following characteristics:

For low-intensity discharges, the ejector acts as an efficient subsonic jet pump entraining a fairly fixed ratio of air thereby increasing the momentum-flux and dilution of the effluent.

For high-intensity discharges, shockphenomena (at the nozzle-exit and possibly along the mixing tube) limit the entrainment but the high velocities provide adequate momentum for subsequent dilution in the external atmosphere.

Self-acting scrubber (Fig 3)

The third system concerns the clean-up of the discharge prior to venting. This is a scrubber in which part of the gaseous throughflow is used to drive a gas-lift pump to provide the liquid counter-flow down through the scrubber packing. The rest of the effluent passes up through the packing.

All of these schemes have the attributes of fluidic systems in that their reliability is high no-matter how long they stay idle awaiting the accident. Many moving-part or electronically activated systems have low standby reliability.

More ambitious fluidic circuits could be proposed but many of these would involve standby power usage. Running costs and vulnerability to power failure would be penalties but these do not afflict the "self-acting" systems suggested here.

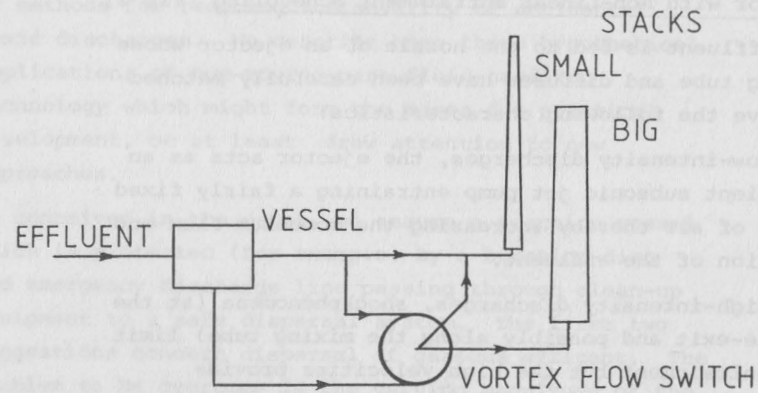


FIG 1

FIG 2

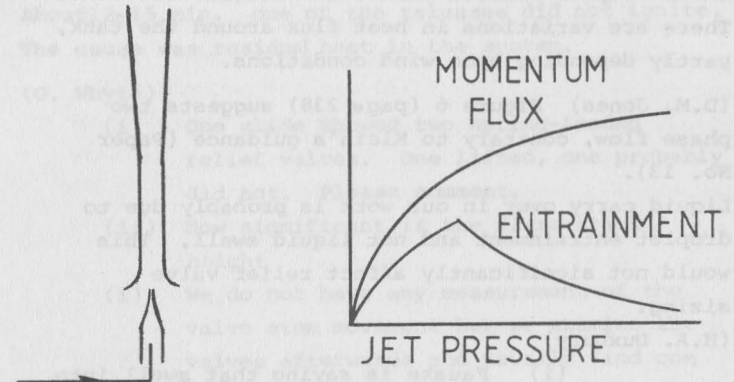
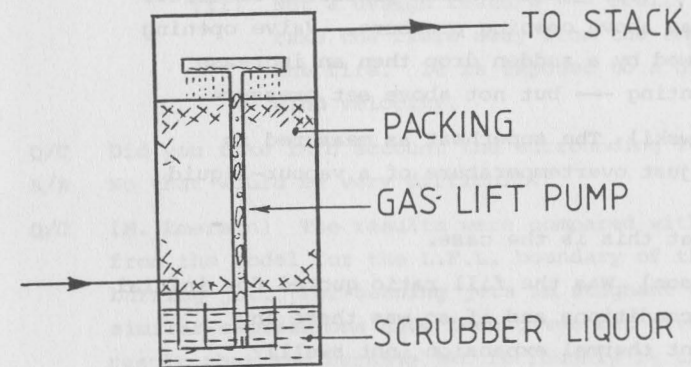


FIG 3



Paper No. 18: Moodie and Jagger

- Q/C (D.K. Cook) Are the convective heat fluxes quoted, average values over the whole tank surface?
- R/A They are from four independent pairs of thermocouples mounted inside and outside the tank. There are variations in heat flux around the tank, partly depending upon wind conditions.
- Q/C (D.M. Jones) Figure 6 (page 238) suggests two phase flow, contrary to Klein's guidance (Paper No. 13).
- R/A Liquid carry over in our work is probably due to droplet entrainment and not liquid swell, This would not significantly affect relief valve sizing.
- Q/C (H.A. Duxbury)
- (i) Fauske is saying that swell into the vent at 80% fill will not occur though it will from a full tank. For flow through relief system "swell" is like liquid but entrainment is little different from vapour.
  - (ii) What maximum pressures occurred?
- R/A No increase above opening pressure. Valve opening was followed by a sudden drop then an increase during venting — but not above set pressure.
- Q/C (H. Kottowski) The superheat as measured is probably just overtemperature of a vapour-liquid mixture.
- R/A Agreed that this is the case.
- Q/C (N. Maddison) Was the fill ratio quoted for initial start-up conditions and if so was there any significant thermal expansion (not swell)?
- R/A Yes, initial conditions but liquid thermal expansion was not significant with the material used.

- Q/C (K. Dixon-Jackson)
- (i) What was the time lag between the extinction of the fire and the two releases which occurred later?
  - (ii) Can you propose a mechanism for this?
- R/A About 12-15 min. one of the releases did not ignite. The cause was residual heat in the system.
- Q/C (G. Whyte)
- (i) One slide showed two spring-loaded relief valves. One lifted, one probably did not. Please comment.
  - (ii) How significant is the flare stack height
- R/A (i) We do not have any measurement of the valve stem movement but we examine the valves afterwards and usually find one is more burnt by the flame than the other. Also we can often relate a sudden pressure drop with a sudden billowing of the flame to indicate valve opening.
- Q/C Is it not worrying?
- R/A Well one valve is often of adequate capacity.
- (ii) Not a design feature — really to take the flare away from the smoke of the fire. It is exposed to a higher wind velocity.
- Q/C Did you take into account the surrounding terrain?
- R/A No that would be very difficult.
- Q/C (M. Emerson) The results were compared with results from the model for the L.F.L. boundary of the non-burning jet. For burning jets in stagnant air similar expressions have been given but give the result that the burning jet is roughly  $1\frac{1}{2}$  times the length to L.F.L. of the non-burning jet. Have the results of your study been compared with the sort of expression which allows for flame temperature etc?

- R/A If you take burning into consideration the model will give a better fit for the data — there is scope in the model to do so.
- Q/C (D.K. Cook) Recent modelling of turbulent diffusion flames has used the concept of a conserved scalar invariant to the progress of combustion. This scalar is related to the fuel concentration but, due to non-linear relationships between the conserved scalar and the composition and temperature within a turbulent diffusion flame any model must account for turbulent fluctuations — usually via a probability density function. Therefore, great care must be exercised when using time-averaged concentrations, as derived from your model, to define a flame profile.
- R/A Yes, I am sure if you take burning into consideration a better fit for the data will be obtained. We are currently studying this aspect.
- Q/C (H.A. Duxbury) Designing on the A.P.I. basis, though not physically right is safe enough. Apart from droplets, the gas is hotter at the top than the bottom of the vessel. Traditionally one would calculate relief requirement assuming the vapour in equilibrium — are you saying that is not safe?
- R/A The vapour is superheated.
- Paper No. 19: Bettis
- Q/C (H. Kottowski) Droplet size is a function of temperature (and thermodynamic equilibrium) so size distribution will change with time. Did you observe this?
- R/A We made no measurements within the cloud except to measure the size. We believe that because of the distance travelled before measurement and the small size that they would have reached equilibrium even if not when leaving vessel. Evaporation is a problem so that droplets did not reach the edge of the pit in which experiments were done (2-3m).

- Q/C (M. Emerson)
- (i) Did you measure any droplet velocities.
  - (ii) Did you attempt to correlate velocity, size and surface tension?
- R/A
- (i) Table 4 (page 260) gives values calculated from the model which agree (order of magnitude) with measured values.
  - (ii) Very complex being affected by evaporation and entrainment into the cloud, etc. — not studied in detail.
- Q/C (R. Duffield) How far apart had the two halves moved in the times for (a) initial pressure drop, 20ms and (b) final pressure drop, 300 ms?
- R/A (b) about 3 cm apart — very slow relative to vapour so having a containing effect so that spread is almost two-dimensional.
- Q/C (J. Munnings) Will research of this kind help designers prevent disasters like Mexico City?
- R/A That is a mechanical engineering rather than fluid mechanics problem. By producing accurate consequence models perhaps, more effort will be directed to design to prevent such incidents.
- Q/C (H.A. Duxbury) Re your first conclusion (page 266); does "major vessel" imply future experiments on a large scale?
- R/A No, "major" refers to vessel failure rather than leakage from cracks etc. We are planning some work involving scale-up for instance exploding of glass spheres in the laboratory.
- Q/C (G.A. Whyte) Would you elaborate on the results in Table 2 (page 259) which indicate decrease in droplet size with increase in percentage of the vessel filled.
- R/A There seems to be an effect but the very limited result is ambiguous and call for further investigation.

Q/C (P.K. Ramskill) Did you calculate theoretically the expected sizes of liquid droplets using the saturated starting conditions and if so, how did they compare with measured values.

R/A Yes, measured values were significantly smaller than predicted theoretically from thermodynamic considerations. We also have a good mechanism for subsequent droplet break-up on exit from the vessel so would not expect this result.

Paper No. 20: Friedel

Q/C (H.A. Duxbury) Some models use the criteria for start of flashing flow so  $L/D = 12$ . For pipe flow we know this is discredited, rather  $L = 100\text{mm}$ . Flow in cracks is probably different because of friction, etc. Could you comment?

R/A Used  $L/D$  because it is used in previous models which we compare. With cracks, even for thin walls  $L/D$  is in range 100 — 1000 and I think length is a better criterion. Next step is to develop a better criterion in a model for pressure drop.

Q/C (H.A. Duxbury) None of the methods are better than 100% (i.e. by a factor of 2). This seems quite good — depends on standard of judgement.

R/A Results are for water only and agreement is not bad — cannot say for other liquids.

Q/C (J.H. Burgoyne) What factors will be taken into account in further research, to improve leakage rate relationships.

R/A Main one is friction factor because of great roughness. One has to modify the roughness/diameter ratio in the Nikuradsee/van Karman equation and to correct for conditions.

Paper No. 21: Cook

Q/C (J.H. Burgoyne)

(i) The problem is radiation intensity falling on surfaces. Reduction in radiative emission with increasing flow rate implies increasing combustion efficiency. Could this be improved by improved flaretip design to improve mixing. There examples of burner designs which improve combustion.

(ii) Has any information been obtained on the effect of water screens in attenuating radiation (relevant to offshore flares).

R/A (i) In gas industry we advice release of gas at highest velocity possible — also better for cross winds but there is the noise problem (except offshore). The Coanda burner is more efficient but is noisy and has a turn-down problem.

(ii) No measurements but we did observe the effect (for about 30s) of turning off the spray curtain on an offshore installation. Another hazard offshore is that although we can accept radiation at  $6\text{kw/m}^2$  for a time, even  $1\text{-}2\text{kw/m}^2$  will bring handrails, etc to a temperature too hot to handle.

Q/C (N.F. Scilly) LNG fires are closer to being emitters at the  $\text{CO}_2$  and  $\text{H}_2\text{O}$  wavelengths than other hydrocarbon fires behaving nearly as black body emitters. The water curtain thus absorbs the wavelengths of the water emission and also causes considerable scatter — probably the more important effect.

R/A Yes and we think it might be better to inject the same amount of water into the flame, provided it does not become unstable. U.S. Bureau of mines

has studied such injection as a means of snuffing out — and have shown considerable reduction in radiation before putting out the flame.

Q/C Steam injection may also be used to reduce radiation.

Q/C (D.A. Carter) Does the multiple point source model assume a constant flame diameter?

R/A When producing the model we considered one to predict the whole flame envelope but this present one is sufficient for the instant radiation level (our interest).

Q/C (M. Emerson) Was the correlation of fraction of heat radiated against velocity done for a single diameter or a range?

R/A A range of diameter from 51 to 590mm. A more sophisticated model would be required to introduce the effect of scale.

Q/C (K. Dixon-Jackson)

(i) Was the composition of the test gas consistently the same as used on the offshore rigs.

(ii) What effect would differences make (e.g. soot on emissivity).

R/A We sample frequently and analyse — it is constant but not the same as offshore. Their gas varies with different operations.

General Survey (J.H. Burgoyne)

The importance of the symposium and the publication of the papers lies in the systematic progress, from the characterisation of unstable substances through the presentation of methods for the study of reaction stability to the problems surrounding discharges. Furthermore we have had a number of papers providing very useful information on specific matters, e.g. the case studies and leakage through cracks. This adds up to a very useful collection of information at the disposal of designers and operators.

Q/C (H.A. Duxbury) Forrest's method was too conservative and is now superseded.

Q/C Where is the boundary between large swell (foaming systems) and small swell.

Q/C (H.A. Duxbury) If in doubt use a large vent for safety.

R/A Yes, often use a safety factor of 2 for foamy systems.

Q/A (A.J. Margetts) Where should a small company go for advice on relief systems?

R/A To my company!

NOTE HSE representatives subsequently showed concern and interest in this problem.