

TRIMONTHLY PROGRESS REPORT

Covering Work from June 6, 1965 through August 27, 1965

to

Dr. H. S. Gardner, Project Coordinator

The Institute of Paper Chemistry

Submitted by

Project 2419

Combustion Engineering, Inc.
Kreisinger Development Laboratory
Windsor, Connecticut

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No. 6 Progress Report on
The Combustion Engineering Program for
Determining the Nature of and Remedies for
Explosive Reaction(s) Between Smelt and
Water in Kraft Chemical Recovery Furnaces

Introduction

The learning process almost invariably produces improvement in an initial theory as experimental work progresses. The development of the encapsulation mechanism theory is no exception. Ideas derived from the heat transfer study in Progress Report No. 5 have permitted changes in the encapsulation theory described in Progress Report No. 4 which make it fit the new information better.

The heat transfer calculations of C-E's No. 5 Progress Report showed that hot water and not steam would be contained in encapsulated water of 0.3 to 3.0 ml volumes after the 0.030 second average induction period for an explosion. A maximum temperature increase of only 60 °F would be realized in this period. The increased internal capsule pressure must then be due to thermal volumetric expansion of liquid water against the containment shell of frozen smelt. Pressure development during even this brief period could be substantial, ranging from 2000 to 6000 psi, as shown by Figure 3 of the heat transfer study.

Rupture of the shell would be a triggering mechanism for the explosive generation of steam produced when liquid water from the fragmented capsule meets molten smelt. The internal pressure developed in the capsule must serve principally to finely disperse the water and propel it at high velocity through the body of molten smelt once rupture occurs. The velocity of the water particles so produced would increase steam production rate by reducing the thickness of the external steam film on each water droplet. This film tends to impede heat transfer. The real explosion then would be due to the explosive generation of steam after capsule rupture placed its liquid water content in intimate contact with the molten smelt.

The tensile strength of the encapsulating shell necessary for an explosion would then have to be sufficient only to contain pressure high enough to effect proper subdivision and ejection velocity of water particles from the ruptured capsule.

The importance of encapsulation may be that it initiates a steam-forming physical explosion like a blasting cap initiates detonation of a chemical explosion of TNT. In each case, a small burst of energy may trigger the development of a much larger quantity of PV (pressure volume) energy from the rapidly expanding gases of the principal explosion.

It may be the case that capsule rupture and the explosive generation of steam from its small water content could initiate further mixing of smelt with "bulk" (non-encapsulated) water above on the surface of the smelt. Mixing of this larger volume of water with smelt would cause an even larger steam explosion.

Within the framework of this evolving physical explosion concept, our laboratory work during the period of this report was primarily concerned with two things:

1. Evaluation of the effect of extraneous sodium compounds other than Na_2S and Na_2CO_3 on the explosiveness of smelt.
2. Evaluation of possible safe quenching agents for the prevention of smelt explosions.

Four commercial recovery furnace explosions have occurred and been investigated by the writer (and others) since the initiation of this project. An attempt to relate pertinent explosion literature and project explosion consultants' opinions to the post-explosion evidence of the four explosions and to our laboratory work is appended to this report. (See Appendix).

Laboratory Experiments

a) Effect of sodium sulfate in smelt on explosive violence

The effect of Na_2SO_4 content of smelt on injection of water or aqueous solutions has been of considerable interest. Earlier work⁽¹⁾ had shown that a 2-10% concentration of Na_2SO_4 in smelt inhibited explosive violence in dissolving tank type quenches in which the smelt was poured into a large volume of water. A series of synthetic smelts of a wide range of sulfidity was made up from Na_2S and Na_2CO_3 to test the effect of Na_2SO_4 on water injection explosions. Each was melted rapidly in a graphite crucible so that reaction of Na_2SO_4 with the carbon crucible would be minimized. Gaseous CO is evolved vigorously by this reaction above about 1850 °F so initial smelt temperatures were kept below this level and the surface of the smelt was observed often to control the temperature. Analyses were made of several smelts which contained Na_2SO_4 before and after melting by the finally chosen procedure to assure that the melting technique did not convert appreciable Na_2SO_4 to Na_2S . Once 1800 °F smelt temperature was reached, the usual 3 ml. successive injections of room temperature water or water solution were made until either an explosion resulted or the smelt solidified. Results are shown in the appended Table 1.

Runs No. 1-3 indicated, as recognized from many previous tests, that Na_2S level must generally be above about 23% (approx. 30% TAPPI sulfidity) for water injections to cause explosions. (This limit was approximately 20% for dissolving tank explosions. However, the minimum % Na_2S for explosions with both kinds of smelt-water mixing is lowered significantly by presence of small percents of explosion intensifiers like NaCl or NaOH in the smelt as discussed further in section (c) or dissolved salts in the quench water.) Presence of 5.7 and 10% Na_2SO_4 did not alter this non-violent behavior as shown in Runs Nos. 2 and 3. Runs Nos. 4 and 5, however, showed that smelt below the threshold Na_2S content (approximately 20% Na_2S , 25% TAPPI sulfidity) containing 5% Na_2SO_4 exploded very violently when either 10% green liquor (10% smelt dissolved in water) or 10% sodium chloride was injected into the smelt. The fact that both NaCl and green liquor produced the same increase of explosive violence indicates that the Na_2S does not have a unique role in intensifying explosions. A better explanation for what appears to be a general property of dissolved salts seems to be the one in C-E

Progress Report No. 5, i.e., that stable salts dissolved in water decrease the life of the vapor blanket separating liquid water from hot smelt in a capsule. This increases heat transfer rate and hence, explosiveness. Explosions resulted from Runs Nos. 6 and 7. These four tests indicate that up to 10% Na_2SO_4 would be inadequate to inhibit explosive violence even in low sulfide smelt if it contacted green liquor formed by the dissolving of smelt by uncontrolled water in the furnace.

Runs Nos. 8 and 9 were made using a different kind of smelt composition. This was low sulfide smelt sensitized with 5% NaCl as might occur with smelt in a mill pulping salt-water borne logs. (Concentrations of up to 12% NaCl were found in the smelt from one such mill.) It exploded on addition of water by both injection and continuous stream addition. The latter term has been referred to as "simulated tube leak" in previous reports. Run No. 10 with this type of smelt containing 10% Na_2SO_4 as inhibitor also exploded, but mildly.

The next series of Runs, Nos. 11 to 16 was made to test Na_2SO_4 over a range of concentrations in moderate to high sulfide smelt (25%-37% TAPPI sulfidity) which is more explosive. All exploded, some very violently, on successive water injections even though Na_2SO_4 in 5.7 to 17.5% was present. Runs Nos. 12 to 16 smelts all lie in a range of Na_2S proportions in Na_2CO_3 which exploded violently without Na_2SO_4 in earlier experiments. Comparing Runs Nos. 1 and 11 indicates that a proportion of Na_2SO_4 high enough may even intensify explosive violence, rather than acting as smelt modifier to reduce explosive intensity.

Data in this Table prove within the limits of experimental procedure used, that sodium sulfate does not act as an explosion inhibitor on injection of either water or 10% water solutions of smelt or NaCl .

b) Effect of sodium hydroxide and sodium oxide in the smelt

A previous progress report by the Babcock and Wilcox research group suggests the possibility of an explosion caused by an exothermic reaction of water with Na_2O , if Na_2O is present in smelt. Because this suggestion implies a non-combustible explosion, a type of explosion of interest in the C-E program, experiments were conducted to indicate the extent to which Na_2O might be present in smelt, and the significance to explosions of the reaction between water and Na_2O .

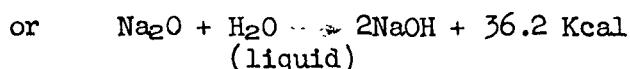
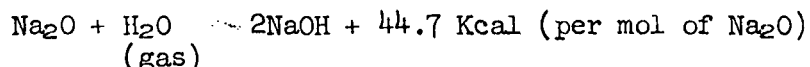
The first series of experiments was arranged to test the effect of graphite crucibles on the formation of NaOH or Na_2O . A 450 gram batch of normal 28% Na_2S smelt was maintained molten at 1600°F and sampled after 15, 30 and 45 minute periods. (Fifteen minutes is the normal holding time on batches for C-E explosion experiments.) No NaOH , Na_2O or elemental sodium, which are grouped together by the TAPPI analysis method, was found by duplicate analyses on each of the three samples.

Another batch of 28% Na_2S smelt, prepared by the regular procedure, was heated in like manner to 1800°F in a graphite crucible. Here again no NaOH or Na_2O was found by analysis after heating for 15, 30 and 45 minutes. When maintained at 1800°F smelt temperature or below, graphite crucibles have not been found to modify the composition of smelt. Smelt melted in crucibles made of ZrO_2 , iron, and graphite gave identical results in explosion tests with water injection. Graphite has

the advantage of being by far the most resistant material to corrosive attack of smelt found by C-E experimenters. Graphite is also cheap and readily available. It has excellent induction heating characteristics. Carbon is a material "native" to the chemical recovery furnace since it composes approximately 50% of char in the ash bed. These desirable attributes and the above experimental results confirm the choice of graphite as a crucible material for smelt explosion test studies.

Suppose Na_2O was produced in smelt by chemical reaction in a furnace bed. What effect would Na_2O have on the explosion behavior of the smelt when it contacted water? These and other questions were to be answered in the next series of experiments. A detailed analysis (1) of carefully taken and preserved samples of smelt from the spouts of 15 kraft mills operating under a wide variety of conditions was made by the writer about ten years ago. The maximum concentration of NaOH plus Na_2O and Na (if present) in any sample was 3.2% on one but the range of all other samples was 0.1 - 1.3%. If higher concentrations of these ingredients had been present in smelt in the furnaces, they must have been volatilized or changed by chemical reaction before reaching the smelt spout.

First, a small pea-sized quantity of pure Na_2O powder (95.7% by analysis) was dropped into about 100 ml. of room temperature water to gain some idea of the explosive violence of pure material on quenching. It combined with water by the following chemical reaction:



Samples of this size and three times as large produced a few bubbles and some warmth, but no real violence. Encouraged by these results we decided to proceed with explosion tests of Na_2O dissolved in a variety of melts. Repeated successive 3 ml. injections of room temperature water were made in each 450g batch of molten material at approximately 1800°F until it either solidified or an explosion resulted. Melting was done in graphite crucibles in the induction heating furnace by the usual technique. Results are shown in Table II.

Runs Nos. 1 to 3 were made with varying proportions of NaOH in Na_2CO_3 . No concentration of NaOH in Na_2CO_3 produced explosions on injections of water into melts of these compositions. Even 100% NaOH did not explode. Runs Nos. 5 and 6 by contrast showed that 15% and 20% sodium chloride in Na_2CO_3 caused violent explosions. These data again emphasized that presence of sulfides is not required for an explosion.

Run No. 7 with 10% Na_2O in Na_2CO_3 , which is about five times the normal level in plant smelt, did not explode on repeated water injections into the molten material. (The Na_2O in this and other experiments was quickly added to already molten 1600°F melt in order to avoid prior reaction with moisture from non-molten ingredients.) The 15% Na_2O in Na_2CO_3 of Run No. 8 exploded very violently. At this point it seemed that enough calibration runs had been made to indicate roughly the lower explosive limit for Na_2O in Na_2CO_3 .

Runs Nos. 9 to 15 were made to compare the effect of Na_2O and NaOH in kraft smelt with that of NaCl . Run No. 9 showed again that 20% Na_2S smelt did not explode with repeated successive water injections. Neither were there explosions in Runs Nos. 10, 11, and 12 when 2% Na_2O , NaOH , and NaCl were added. The same kraft smelt containing 5% Na_2O exploded violently in Run No. 13, but 5% NaOH in Run No. 14 and 5% NaCl in Run No. 15 also sensitized the smelt and produced the same order of explosive violence.

It is concluded that neither Na_2O nor NaOH in concentrations normally found in smelt (up to about 2%) was sufficient to make 20% Na_2S smelt explode violently. Sodium chloride at 2% gave the same results. Sodium oxide at 5% in 20% Na_2S smelt sensitized it enough to produce violent explosions. Both 5% sodium hydroxide and 5% sodium chloride, however, produced the same violence as 5% sodium oxide in the same smelt.

From these experiments it appears that no unusual hazard would be presented by sodium oxide in kraft smelt at normal concentrations. At up to about four times the normal concentration, the effect of Na_2O was indistinguishable from that of the same proportion of NaCl or NaOH . Due to these results and the discovery that no detectable Na_2O , Na , or NaOH was created by the normal melting procedure for smelts in graphite crucibles, we feel that Na_2O , Na , and NaOH played no part in the violent smelt-water explosions under nitrogen atmosphere in the spherical test vessel which were described in the last C-E progress report.

c) Effect of sodium chloride combined with high sodium sulfide in smelt on explosion inhibition by quench solutions

Considerable attention has been devoted to aqueous quenching solutions because they still appear to offer the possibility for developing a safe commercially-feasible method for shutting down a recovery boiler rapidly should a water leak develop in the furnace. Results and discussion of experiments on quenching agents have been presented in the last four C-E progress reports.

Injection of quenching solutions into smelt has been used in most experiments because this method of mixing provides the most violent and consistent explosions with water. Thus injection represents the most drastic laboratory condition known for mixing smelt and water. If a quenching solution prevents explosions when injected into smelt under a wide variety of conditions, it is considered a good candidate for further study. But only after passing all tests without any kind of explosion would it be recommended for furnace testing.

Although 10% aqueous ammonium sulfate solution succeeded in inhibiting smelt explosions under a wide variety of simulated plant conditions described in the last progress report, it had not until recently been tried on high sulfidity smelt which contains sodium chloride, a smelt composition known from previous work to increase greatly the violence of smelt-water explosions.

A series of smelt compositions containing high Na_2S content, above about 23%, was made up to contain NaCl . A succession of 3 ml. injections of water or aqueous solution was made into each molten 1800°F

smelt until an explosion or solidification of smelt resulted. The outcome of these experiments is reported in Table III. Run No. 1 showed that high sulfidity smelt with 5% NaCl explodes violently on water injection. (It does also without NaCl). Run No. 2 confirmed previous data of C-E Progress Report No. 5 in illustrating that explosions with low sulfide smelt containing 5% NaCl are inhibited successfully by 10% ammonium sulfate solution.

Runs Nos. 3, 4 and 5, however, showed that the combination of high sulfide with even 1% NaCl was not inhibited by 10% ammonium sulfate, the most promising candidate developed to that time. Runs Nos. 6 and 7 (the latter run in duplicate) on the new standard smelt with high sulfide and 5% NaCl showed that 10% ammonium bicarbonate did act as an inhibitor where 10% ammonium sulfate had failed. It was reasoned that this contrasting behavior might be due to the difference in rate at which the two compounds form a vapor blanket on contact with hot smelt. (Chloride-containing smelt may be able to develop more rapidly an encapsulation shell strong enough to allow build-up of water-dispersing pressure since it is believed to be a stronger per unit thickness than smelt which contains no chlorides.) Runs Nos. 8 and 9 were hence made with ammonium hydroxide which has a high vapor pressure at relatively low temperature. The 9% (by weight as NH_3) ammonium hydroxide solution did successfully inhibit explosions but, like ammonium bicarbonate, it might pose in-plant problems due to lack of stability on storage. Runs Nos. 10 and 11 showed that almost the same concentration of ammonium hydroxide would be necessary when combined with 10% ammonium sulfate solution.

Next it was decided to try the effect of increased concentrations of ammonium sulfate in water solution. The 15% concentration at room temperature in duplicate runs No. 12 inhibited explosions with chloride-containing smelt. When chilled to 40°F in Run No. 13, however, it gave a mild explosion probably due to the decreased rate of ammonia vapor production. Chilling was used to approximate conditions of use in a plant with outdoor storage of quench solution. Further increase in concentration to 20% at room temperature in Run No. 14 inhibited explosions in duplicate experiments. At this point it was reasoned that the safest ammonium sulfate solution to use in a furnace would be the one capable of safe quenching after greatest dilution with boiler water from a tube leak. A forty per cent solution, which is the limit of solubility of this salt at 32 °F, was chosen for further tests. Run No. 15 at room temperature and No. 16 at 212°F, showed that 40% $(\text{NH}_4)_2\text{SO}_4$ successfully inhibited explosions over this temperature range.

Run No. 17 showed that 40% solution worked even with 10% NaCl dissolved in the smelt. Runs Nos. 18 and 19 showed that 40% solution also was effective at 140°F and 32°F. Runs Nos. 20 and 21 showed that 40% solution successfully inhibited the most violent quenching smelt to date (with 10 and 15% NaCl, and high sulfide) even when the solution was chilled to 36-38°F before injection.

It would seem in tests to date that 40% ammonium sulfate could inhibit any plant smelt composition with which we are familiar. More tests under a wide variety of simulated furnace conditions, however, must be run before a definite recommendation can be made.

d) Effect of anion type in quench solutions

It was a natural point of curiosity to wonder if some other ammonium compound or gas-producing chemical would inhibit explosions better than ammonium sulfate. A series of previously untried compounds was made up in water solution and injected in 3 ml increments into very high sulfide smelt with no chloride by the standard test procedure used in other experiments. Results are shown in Table IV.

The 10% ammonium sulfate solution successfully inhibited explosions, while 5% produced a surge showing border-line effectiveness. The 5% NH_4Cl of Run No. 4, by contrast with 5% $(\text{NH}_4)_2\text{SO}_4$, gave a violent explosion. The 10% NH_4Cl of Run No. 5 gave a mild explosion as did also Run No. 6 with 10% NH_4Br , another halide. All halides tried to date in either the smelt or in quenching solutions have increased explosion violence. Ammonium acetate in Run No. 7 was an effective inhibitor. It has poor stability on exposure to air and offers no known advantage over $(\text{NH}_4)_2\text{SO}_4$. In Run No. 8 the 10% ammonium bisulfate solution, which had a strongly acid reaction in water, was also effective. This suggested that dilute sulfuric acid might also work since it would generate gases (CO_2 and H_2S) on contact with smelt. Such was the case if the acid were strong enough as demonstrated in Runs Nos. 10 and 11.

At present no advantage of acid solutions is recognized. Storage and transfer to the furnace might cause corrosion problems. Pure ammonium sulfate in 10% solution is slightly acid with a pH of 6.0. In another experiment not shown in this table, the addition of enough sulfuric acid to adjust the pH of 10% $(\text{NH}_4)_2\text{SO}_4$ to 3.3 (as might occur with impure commercial grade material) did not decrease its effectiveness. Buffering ammonium sulfate solution with enough ammonia to put it on the alkaline side, about pH 9, would protect the tanks and lines from corrosion. This small proportion of free NH_4OH would be expected to slightly increase explosion inhibition.

Run No. 12 with 5% ammonium sulfamate, $\text{NH}_4\text{SO}_3\text{NH}_2$, a fire retardant material with high thermal decomposition point, 320°F, did not work and neither did urea in Run No. 14 which decomposes above 270°F. The 10% sodium sulfate solution of Run No. 13 caused an explosion. This agrees with the analysis of a furnace explosion reviewed by the writer in which salt cake in water solution (rather than in black liquor) had been sprayed into the furnace bed. The 10% ammonium bicarbonate inhibited explosions in duplicate Runs Nos. 15 and 16. It has a high gas-producing capacity but is thermally unstable in dry form and specially in aqueous solution. The dibasic ammonium citrate was a successful inhibitor at either 10% or 5% in Runs Nos. 17 and 18 but has the disadvantage (compared with ammonium sulfate) of less stability and more cost.

To date there appear to be three serious candidates for further study: ammonium sulfate, ammonium hydroxide, and ammonium bicarbonate. We are concerned that the latter two solutions applied to the ash bed and smelt in a furnace may have too much volatility of active ingredient, i.e., that they may lose gas supply too rapidly on contact with hot furnace gases or alkaline char to retain enough for safe quenching of molten smelt below, which is the real problem. Only further testing can establish whether this is a valid criticism.

Discussion of Quenching Agents

How much quenching solution would be necessary to cool the molten smelt to a safe temperature in a 20' x 16' 300 ton C-E decanting bottom furnace? Mr. L. J. Jacobs of C-E made a number of assumptions in performing the following calculation. For instance, the sensible heat content of the ash bed was disregarded. A 3.82" depth of molten smelt was assumed over the entire bottom of the furnace. Furnace hearth dimensions of 19' 5/8" x 15' 9 5/8" were taken to correspond with an actual contract. The smelt would be cooled only to the solidification point, 1430°F. This would require approximately 263 gallons of aqueous quench solution or 2200 lb, assuming heat removal was not affected by the dissolved $(\text{NH}_4)_2\text{SO}_4$. The water of the solution would generate about 60,000 ft³ of steam at 212°F which would be expected to provide an inert atmosphere for combustion reactions, especially in the bottom of the furnace. Chemical reactions in the bed like pyrolysis of black liquor and the water gas reaction would probably be quenched speedily by spraying liquid water solution on the bed, since aqueous solutions have a high heat capacity.

What makes some aqueous chemical solutions non-explosive on injection into molten smelt? The answer seems to lie in their ability to create large volumes of gas quickly on contacting smelt. The gas production necessary for a successful aqueous quenching agent can come from several types of reactions: (a) the production of vapor by volatilization of a high vapor pressure material like ammonium hydroxide, volatile compounds like acetone and methyl alcohol, or even hot water above 187°F. (b) the chemical reaction of smelt with aqueous solutions like dilute sulfuric acid (to give CO_2 and H_2S) or ammonium sulfate (to give ammonia) or (c) the thermal decomposition of compounds like ammonium bicarbonate (which yields H_2O , CO_2 , and NH_3).

The gas blanket provided inside the capsule by such quenching agents is believed to decrease the rate of heat transfer from the molten smelt to water inside the capsule and hence also the thickness of the surrounding frozen smelt and the temperature of the encapsulated water. In addition we believe this gas blanket provides a compressible volume inside the shell which is able to absorb thermal expansion of the encapsulated liquid water without great increase in internal capsule pressure. The presence of this enveloping gas film around the enclosed volume of water would thus decrease the chance of an explosive encapsulation. A vapor blanket would decrease the build-up of water-atomizing pressure if a water-containing capsule did form and rupture.

Quenching agent candidates can now be chosen easier since several tentative criteria have been established which simplify selection. For instance, a quenching agent ideally should: (1) generate large volumes of non-flammable, non-toxic gas readily on rapid heating in aqueous solution below 212°F or on chemical reaction with smelt, (2) have sufficient stability in aqueous solution to allow long-term storage in metal tanks over a range of temperatures normal to in-plant and outdoor conditions, (3) leave no residue on application to smelt which will contaminate the chemical recovery system, (4) be highly soluble in water, and (5) be cheap, non-toxic, stable on storage in solid form, non-corrosive, and readily available in commercial quantities. Some of these qualifications can obviously be sacrificed if the material is an effective enough inhibitor.

Future Work

Work in the final four months of the project in 1965 will concentrate primarily on the development of practical remedies for smelt explosions in furnaces. The mechanism studies have provided several clues to measures which could possibly prevent explosions in the field. Areas to be covered include the following:

- 1) The application of aqueous quench solutions to the smelt and ash bed as soon as a tube leak is discovered. (A good automatic system for leak detection would add considerable utility to this system.) The three candidates mentioned earlier, ammonium sulfate, ammonium bicarbonate, and ammonium hydroxide will be screened extensively by tests which simulate a wide variety of furnace conditions. Some of the variables to be studied are the effect of smelt composition (Na_2S , NaOH , and NaCl), presence of ash bed and black liquor, tests on samples of plant smelt from several mills, method of addition of quench solution, and a detailed analysis of decomposition products, both gases and solids. Additional quenching agents will be screened concurrently as they come to our attention.
- 2) The tendency of black liquor itself to explode physically in contact with smelt will be explored more thoroughly above the 35% maximum solids concentration which exploded in previous tests. New means of injecting heavy liquors will be tried in order to determine more exactly the upper concentration (and inorganic salt content) which can explode under the best possible mixing conditions. The effect of strong black liquor applied to the surface of smelt on cooling rate and accessibility to water will also be studied.
- 3) A limited additional number of smelt additives to modify its explosiveness on contact with water will be tried. Fifteen are on hand ready for testing.
- 4) A scale up of water quantities from 5 ml. maximum at present in the plywood booth to 50 or 100 ml. should be made in the spherical vessel in order to get a better idea of the pressure signature of larger explosions more characteristic of those in an operating furnace. Such data would be useful in the stress analysis study of furnace explosions being made by Mr. R. Robinson at Illinois Institute of Technology Research Institute.

Completion of these additional studies should allow us to make definite recommendations about remedial measures worthy of study in a black liquor-fired semi or full scale furnace. This may be the next step beyond the present research contract.

Conclusions

- (1) Under proper circumstances molten smelt can react physically with submerged liquid water very rapidly to produce steam explosively.
- (2) Sodium sulfate in the smelt does not inhibit physical smelt-water explosions.

- (3) The normal procedure for preparing experimental smelt in graphite crucibles does not produce significant quantities of Na_2O , NaOH , or elemental sodium.
- (4) The presence of Na_2O , NaOH , or NaCl in laboratory smelts results in equivalent behavior on contact with water indicating that no unusual explosive contribution is to be expected from the presence of Na_2O .
- (5) High sulfide smelt (above about 25% Na_2S) with sodium chloride is a particularly explosive composition hard to inhibit by quenching solutions. The 40% ammonium sulfate solution in water, either hot or cold, successfully quenched high sulfide-chloride smelts. More work on this and other quenching solutions will be necessary before a recommendation for plant trial can be made.

Expenditures on the C-E Smelt-Water Explosion Study

Costs (cumulative) of the Combustion Engineering, Inc. study as of July 31, 1965 are itemized as follows:

Labor	\$ 36,950
Overhead	57,850
Materials	<u>47,200</u>
Total	\$142,000

A graph showing the rate of expenditure is appended.

Wharton Nelson

WHARTON NELSON
Senior Project Engineer

Charles L. Norton
CHARLES L. NORTON
Research Engineer

August 28, 1965

TABLE 1

Effect of Na₂SO₄ in Smelt

	<u>% Na₂S</u>	<u>Other</u>	<u>% Na₂SO₄</u>	<u>Quench Solution</u>	<u>Explosion</u>
1.	22.9			Water	None
2.	17.9		5.7	Water	None
3.	16.9		10	Water	None
4.	19.7		5	10% Green Liquor	V*
5.	19.9		5	10% NaCl	V*
6.	20.6		10	10% Green Liquor	V*
7.	16.5		5	10% NaCl	Moderate
8.	20.4	5NaCl		Water	V*
9.	19.3	5NaCl		Continuous stream addition	Moderate
10.	17.2	5NaCl	10	Water	Mild
11.	21.4		17.4	Water	V*
12.	25.9		5.7	Water	Moderate
13.	25.3		10	Water	V*
14.	25.4		9.1	Water	Mild
15.	27.5		6.1	Water	VV*
16.	30.1		17.5	Water	V*

* Crucible shattered by explosion

V is violent

VV is very violent

TABLE II

Effect of NaOH, NaCl, and Na₂O in Melts
(3 ml. injections of water were used in each case)

<u>Melt, % Composition</u>	<u>Explosion</u>
1. 15 NaOH - 85 Na ₂ CO ₃	Surge
2. 20 NaOH - 80 Na ₂ CO ₃	None
3. 50 NaOH - 50 Na ₂ CO ₃	Pops
4. 100 NaOH	Violent Spitting
5. 15 NaCl - 85 Na ₂ CO ₃	V
6. 20 NaCl - 80 Na ₂ CO ₃	V
7. 10 Na ₂ O - 90 Na ₂ CO ₃	None
8. 15 Na ₂ O - 85 Na ₂ CO ₃	VV*
9. <u>20% Na₂S smelt</u>	None
10. <u>2 Na₂O - 20% Na₂S smelt</u>	None
11. <u>2 NaOH - 20% Na₂S smelt</u>	None
12. <u>2 NaCl - 20% Na₂S smelt</u>	None
13. <u>5 Na₂O - 20% Na₂S smelt</u>	V*
14. <u>5 NaOH - 20% Na₂S smelt</u>	V*
15. <u>5 NaCl - 20% Na₂S smelt</u>	V*

* Crucible shattered by explosion
V is violent
VV is very violent

TABLE III

Effect of NaCl and High Sulfidity on Inhibition

<u>Runs</u>	<u>% Na₂S</u>	<u>% NaCl</u>	<u>Injections **(3 ml)</u>	<u>Explosion</u>
1.	28.1	5	Water	VV*
2.	18.5	5	10% (NH ₄) ₂ SO ₄	None
3.	26.4	5	"	V*
4.	25	3	"	V*
5.	25	1	"	VV*
6.	27.8	5	5% NH ₄ HCO ₃	V*
7.	25, 27.2	5	10% NH ₄ HCO ₃	None
8.	25.7	5	4.5% NH ₄ OH	V*
9.	27.9	5	9% NH ₄ OH	None
10.	25	5	10% (NH ₄) ₂ SO ₄ , 3% NH ₄ OH	Moderate*
11.	25	5	10% (NH ₄) ₂ SO ₄ , 9% NH ₄ OH	None
12.	25, 25	5	15% (NH ₄) ₂ SO ₄	None
13.	28.2	5	<u>40°F</u> 15% (NH ₄) ₂ SO ₄	Mild*
14.	27.3, 25	5	20% (NH ₄) ₂ SO ₄	None
15.	27.0	5	40% (NH ₄) ₂ SO ₄	None
16.	26.6, 27.5	5	<u>212°F</u> 40% (NH ₄) ₂ SO ₄	None
17.	27.1	10	40% (NH ₄) ₂ SO ₄	None
18.	28.2	5	<u>140°F</u> 40% (NH ₄) ₂ SO ₄	None
19.	25.7	5	<u>32°F</u> 40% "	None
20.	26.6	10	<u>36°F</u> 40% "	None
21.	25.8	15	<u>38°F</u> 40% "	None

* Shattered crucible

** Made with room temp. (80°F)
solution unless stated otherwise.

TABLE IV
EFFECT OF ANION

<u>Run</u>	<u>% Na₂S Smelt</u>	<u>Aqueous Quench Solution</u>	<u>Explosion</u>
1	30	5% (NH ₄) ₂ SO ₄	Surge
2	"	10% "	None
3	"	" "	None
4	"	5% NH ₄ Cl	V*
5	"	10% "	Mild
6	"	10% NH ₄ Br	Mild
7	"	10% NH ₄ Acetate	None
8	"	10% NH ₄ HSO ₄	None
9	"	"	None
10	"	0.5% H ₂ SO ₄ (N/10)	Mild
11	"	5% H ₂ SO ₄	None
12	"	5% NH ₄ Sulfamate (NH ₄ SO ₃ NH ₂)	Mild
13	"	10% Na ₂ SO ₄	Mild
14	"	10% Urea (NH ₂) ₂ CO	VV*
15	"	10% NH ₄ HCO ₃	None
16	"	"	None
17	"	10% Dibasic NH ₄ citrate	None
18	"	5% Dibasic NH ₄ citrate	None

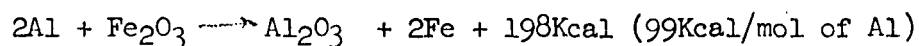
* Shattered Crucible
V is violent
VV is very violent

APPENDIX

Preliminary Analysis of Recovery Furnace Explosion Damage

(a) Shock waves developed by smelt-water explosions

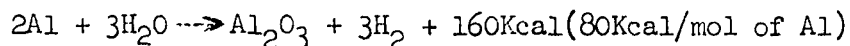
A chemical reaction to be explosive must have three characteristics⁽²⁾. The heat of reaction is a criterion of the efficiency of the explosive material and is its most important characteristic. Thus a chemical reaction must be highly exothermic to be explosive in nature. Second, it must take place at a high rate, which distinguishes normal chemical reactions from explosive ones. Finally, a chemical reaction must form a gas. For instance, the following well-known thermite reaction is rapid and highly exothermic, but does not form a gas. It hence does not explode.



It can therefore be concluded that only the simultaneous combination of these three basic factors: exothermicity, high process rate, and gas formation, can guarantee a chemical type explosion.

Higgins and Schultz⁽³⁾, in their thorough study of molten metal-water interactions which might take place in case of a run-away nuclear reactor, described a number of interesting results which seem to contrast with those from the present study. They mixed intimately the molten metals, uranium, zirconium, aluminum, sodium-potassium alloy, and stainless steel with water under various conditions and recorded the pressure waves and other variables in a highly instrumented system. Mixing was accomplished by spraying the molten metals into water and also by finely dispersing molten metal submerged in water with a blasting cap. With the two methods of mixing, the results were equivalent when particle-size distribution was approximately the same.

Higgins and Schultz state that the chemical reaction of molten aluminum with water (which occurs if the metal is very hot and finely divided) is highly exothermic and produces hydrogen, and that the reaction is nil up to 2138°F. (The melting point of aluminum is 1220°F.)



The proportion of aluminum reacting with water (approx. 60%) was higher than for other metals tested.

Higgins and Schultz recorded the pressure rise times on oscillograms (reproduced as Figure 1). To quote them:

"The pressure pulses measured in the explosion dynamometer were primarily due to the liberation and expansion of the hot hydrogen gas....."

"In observing the pressure rise time, it is evident that the

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metal-water reactions are not high-order explosions -- taking milliseconds rather than microseconds to attain peak pressure. The metal-water reactions could be described as deflagrations instead of detonations, but are slightly more brisant than black powder, as indicated by the rates of pressure rise..... From the above considerations and from the absence of shattering-type damage, it was concluded that the effect of shock waves was not important in these tests."

Contrast these rates of chemical reaction of molten metals and water with the pressure signature (pressure versus time trace) of a typical C.E. laboratory smelt-water physical explosion reproduced as Figure 2. It can readily be seen that physical smelt-water explosions: (1) average 0.1 to 3 milliseconds and are hence 5 to 300 times faster, (2) have much faster rise and decay times, and (3) are of an entirely different type from deflagrating chemical reactions of molten metals with water. The wave from a smelt-water explosion by contrast is a shock wave produced from explosively-generated steam. This concept is discussed in more detail in the section which follows.

The violent smelt-water explosions in nitrogen atmosphere described in C.E. Progress Report No. 5 ruled out combustion as an explanation for these laboratory explosions.

(b) Inspection of four explosions

The distribution of damage in all four chemical recovery furnace explosions inspected by the writer during the course of this study has been of the same general pattern but the explosion intensity has varied widely. Two of them produced little easily-evident damage in the furnace up to an elevation one floor above the operating level (approx. 25' above the molten smelt level). Here and above the buckstays became bulged on all four sides. Corner bolts above this level were broken in the case of powerful explosions. In three out of four cases, the corners of the furnace above the operating floor generally split open vertically as designed to meet severe pressure surges. The economizer casing usually was opened. In two of the four explosions substantial (1"-4") deflections were noted in heavy I beams under localized areas of the furnace bottom. Beams were not measured after the first two explosions.

An unusually severe series of multiple explosions occurred over a four minute period in one furnace. The smelt was cleaned thoroughly from the surface of floor tubes in the entire bottom. Two highly localized dish-shaped depressions about a yard in diameter were found in the floor tubes. One, 4 1/2" deep, was near the left rear corner. The other, also 4 1/2" deep, was near the middle of the furnace front close to the center smelt spout. The corner depression matched an approx. 5" localized outward displacement of adjacent vertical water wall tubes extending upward about 4'. The left rear vertical corner (only) of the furnace was ripped open over a 6' vertical distance starting 3' above smelt

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level. The 14" wide flange I beams beneath the furnace floor had been deflected 2 1/2 to 4". The furnace roof was opened and minor casing damage to the economizer was incurred. On hydrostatic testing the furnace, a number of leaks were found where wall tubes had been torn loose from welds to channels directly above the corner floor depression. Correspondingly, the depression near the center of the furnace floor matched the location where the ripped smelt spout "can" is believed to have placed water in the molten smelt.

Two consultant explosion specialists examined the damage in this furnace and agreed that the energy density required to create the depressions was far above that which would have been produced by a combustible gas mixture. (4)

(c) Theory on distribution of furnace damage

It is believed that the damage in three furnace explosions and major damage in the fourth was due to a physical smelt-water explosion mechanism. These explosions liberated high density PV energy (in the shock wave range) in a limited area of the furnace bottom where water contacted molten smelt. The decaying explosion pressure wave then spread through the remainder of the furnace structure. The general pattern of damage on furnace structures which at first glance might suggest gas explosions high in the furnace, may instead be the result of the distribution of furnace containment strength and the effects of either a shock wave alone or a shock wave combined with a rapid pressure rise similar in characteristics to a combustible explosion.

In a significant number of chemical recovery furnace explosions, we believe that the distribution of damage observed could not have been caused by a rapid increase in pressure of the total furnace atmosphere in such a large enclosure. In these cases, the distribution of damage can best be accounted for on the basis that it was caused by a shock wave with or without a deflagration wave.

From a study of the available literature, the large scale liberation of flammable gas by chemical reaction of molten smelt and water (if such occurred in a furnace) and its subsequent ignition could not have caused such a shock wave. This follows from the fact that ignition of a limited amount of flammable gas in a furnace would not result in a detonation but rather in a deflagration type of explosion which would not produce a shock wave. A deflagration wave, which can produce a maximum of about 150 psi pressure increase, travels at subsonic speed. Hot gaseous products from the explosive combustion of a flammable gas mixture expand and create a pressure increase through the whole volume of the container. This would hence distribute pressure rather evenly to nearby walls of the furnace.

The postulation that damage was created by a shock wave from the explosive production of steam in chemical recovery furnaces is supported by several observations. These include the following:

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- 1) Localized depressions in the floor tubes which could not have been created by combustible gas explosions.
- 2) Since no visible flames were observed to issue from furnace openings in the four recent explosions, a combustible gas explosion is not indicated. Some explosions occurred while there was an actively burning bed in the furnace.
- 3) The significant deflections of heavy I beams beneath the furnace could not be caused by explosion of combustible gas mixtures. The development of pressure from a deflagration explosion would cause opening of the furnace corners which would relieve the pressure before significant floor beam deflection could occur.
- 4) From the accounts read, the nature of and damage from plant explosions caused by introducing molten steel, aluminum, and cobalt, as well as molten non-metals like bauxite (Al_2O_3) and sodium chloride into water is strikingly similar to that from smelt-water explosions. None of these former explosions could be attributed to the formation and subsequent oxidation of a flammable gas.

Shock waves, like sound, have directional effects. They can be reflected from surfaces and when wave fronts coincide after reflection, a more powerful force may be applied to a localized area. Shock waves of numerically small pressure magnitude per square inch can create significant damage, as illustrated by data of the following table (5).

<u>Over-pressure* in Shock Wave, PSI</u>	<u>Damage</u>
0.5 to 1.0	Shatters glass windows.
1.0 to 2.0	Shatters corrugated asbestos siding. Corrugated steel or aluminum paneling fails and buckles.
2.0 to 3.0	Concrete wall panels, 8 or 12 inches thick (not reinforced) shatter.
2.5	Moderate damage to light steel frame industrial buildings.
4.0	Moderate damage to medium steel frame industrial buildings and to wall bearing, brick buildings.
5.5	Moderate damage to steel frame office type buildings and to reinforced concrete frame and wall multi-story buildings. Severe damage to wall-bearing brick buildings.

* Pressure above atmospheric

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How can a physical smelt-water explosion in the bottom of a furnace result in damage far above to the casing, corners, refractory, and even in the economizer? Another part of the answer may lie in the distribution of structural strengths in various part of the furnace itself. The bottom and lower welded furnace walls are much stronger than the upper walls and economizer casing. The furnace roof in many designs is also strong. It may be a correct analogy to compare resistance to explosion force between a shot gun with muzzle plugged by mud and a furnace with a smelt explosion in the bottom. In the former case, the muzzle often "banana peels" i.e., splits in several longitudinal sections when fired, while the breech where the shell was exploded remains intact because of its greater tensile strength produced by thicker metal. These opinions should not be assumed to take issue with current furnace design, since it would be technically infeasible to design an explosion damage-proof furnace.

The fact that all explosions to date have been described as "muffled" or "rumbling" probably reflects the sound-deadening effect of the heavier - armored bottom location in which they are believed to occur. (Lab explosions give a short "crack" which implies high velocity. Transducer pressure traces of the shock waves reinforce this view.) The proposed hearth area location of these explosions may provide an explanation also for the extremely low injury rate of personnel who usually work at the smelt spout or operating floor elevations of the recovery furnace.

No chemical recovery furnace explosion to date has been observed by those nearby to expel flames from the furnace openings, although this question is always asked. The operators usually refer only to blinding clouds of steam and finely divided black ash driven from the smelt spouts, liquor gun openings, and fissures in the casing created by the explosion.

For the reasons outlined in this section, it is believed that all four explosion sites recently inspected by the writer involved contact of water or some aqueous solution (other than strong black liquor) with molten smelt. Such explosions are believed to have been physical smelt water explosions which generated shock waves.

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- 5) "The Effects of Nuclear Weapons," U. S. Atomic Energy Commission 1962.

RESULTS OF AEROJET EXPLOSION DYNAMOMETER TESTS

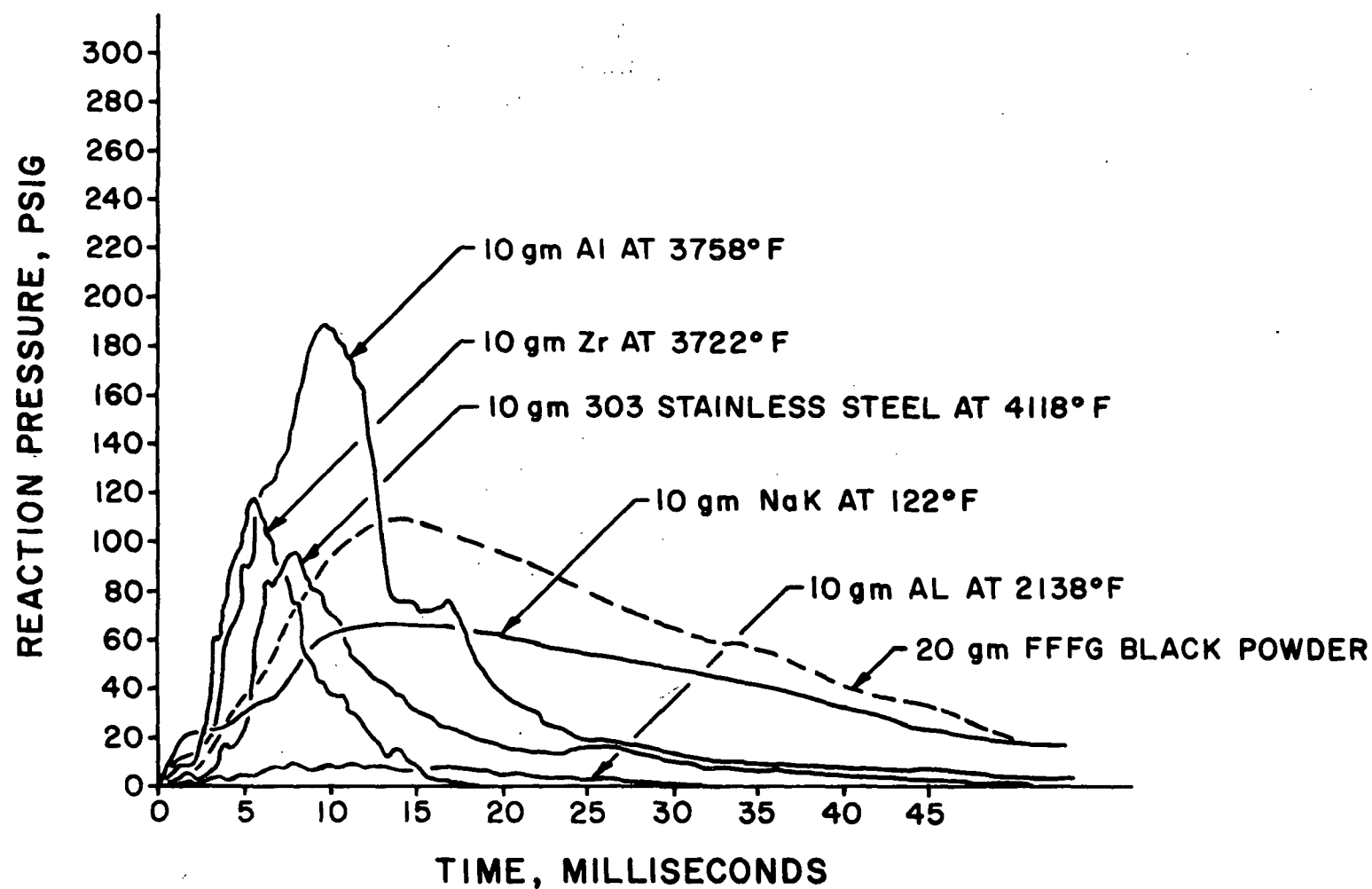


FIGURE NO. 1

Data From Higgins And Schultz
Reference No. 2

TYPICAL TIME - PRESSURE TRACE OF A SMELT - WATER EXPLOSION

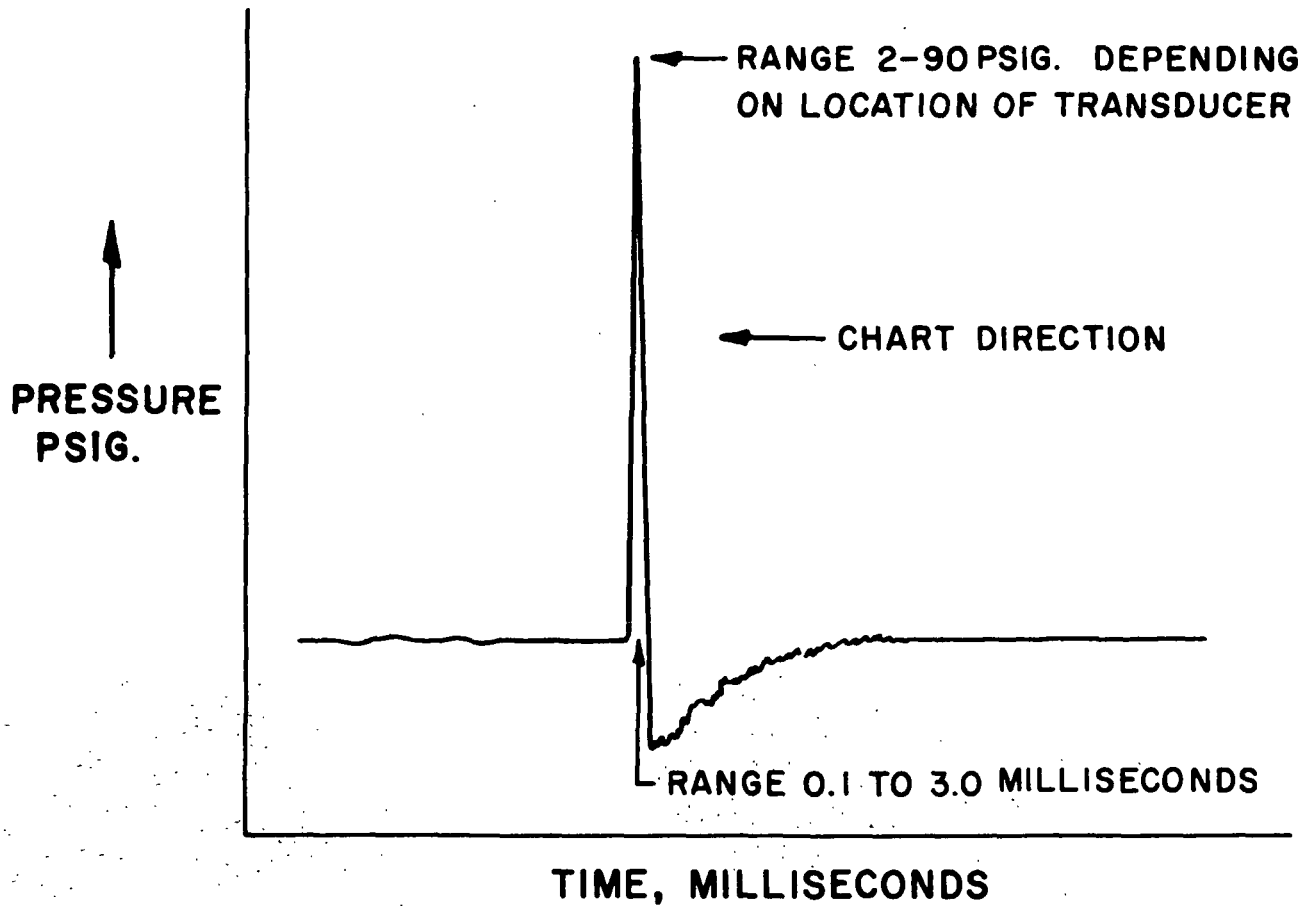


FIGURE NO.2

CUMULATIVE EXPENDITURE - THOUSANDS OF DOLLARS

