F. LH76

DEVELOPMENT OF THE MOLTEN CARBONATE PROCESS TO REMOVE LEAD AND OTHER PARTICULATES FROM SPARK IGNITION ENGINE EXHAUSTS

Atomics International
North American Rockwell

P.O. Box 309
Canoga Park, California 91304

CONTRACT: CPA 70-3

CONTENTS

EPI 000238

TABLES

FIGURES

EPI 000239

I. SUMMARY

The effectiveness of a molten alkali carbonate eutectic in removing lead compounds from gaseous mixtures was investigated. Some laboratory tests and one test of a device on an automobile were used in this investigation; results indicated that molten alkali carbonate scrubbers can be an effective method for removing lead and particulates from exhaust. The alkali metal carbonate eutectic is a basic low-melting, nonviscous, clear liquid that reacts chemically with acidic lead exhaust components and physically wets particulate matter.

Tests have shown that the size of the lead chloride particulates produced in laboratory generation experiments approximated those found in automobile exhaust. The size of the particulates from a cooled gas stream varied from 0.01 to 5μ. In general, particulates from 0.1 to 1μ in size predominated. It was found that increasing concentrations of lead chloride vapor produced particulates of larger average size.

Both impingement of the gas on the molten salt surface and contacting the gas with molten salt wetted-mesh scrubbers were shown to be effective lead removal techniques. The lead removal efficiency in a wetted-mesh scrubber increased as the gas residence time in the wetted-mesh increased, and decreased as the gas velocity through the mesh increased. Over the temperature range measured (430 to 500°C) the lead removal efficiency in a wetted-mesh scrubber increased as the melt temperature decreased. This temperature dependence would not be expected for lead chloride vapor, but is not unreasonable if some of the lead chloride condensed to particulates at lower temperatures. In a wetted-mesh scrubber the removal efficiency was essentially independent of the lead particulate concentration in the gas stream over the small concentration range measured. The fraction of lead removed after impingement against a molten salt surface increased as the impingement velocity increased. In addition, over the temperature range measured removal by impingement was more effective as the temperature decreased.

These results suggest that a muffler replacement device could potentially remove nearly all of the lead from the exhaust. A conceptual device that could be retrofit to existing automobiles was designed. This conceptual muffler replacement unit would cost about $20 to fabricate and charge with salt. Salt

EPI 000240

replacement would be required every 15,000 to 30,000 miles; at current prices, each salt charge would cost ~$2. Considering normal commercial markup, total consumer cost for emission control by this method is estimated to be <1¢/gal or <1 mill/mi. It is estimated that this unit will remove >93% of the lead, >99% of the sulfur oxides, and >80% of the particulates in all operating modes of an automobile.

Tests of a preliminary molten carbonate device on an automobile (designed, constructed, installed and tested on a company vehicle at company expense prior to contractual obligations) were carried out in both start-stop street driving and high-speed freeway driving cycles. About 60 to 70% of the total particulates, 85 to 95% of the lead, and ~5 to 30% of the nitrogen oxides were removed from the exhaust in the molten salt scrubber. (Up to 80% of the nitrogen oxides have been removed in an additional catalyst bed.) These results showed that even before the melting temperature of the salt was reached, the demisting mesh and/or the salt on the mesh removed 80% of the lead from the exhaust. Redesign and testing of a second device (funded at company expense) has resulted in improved lead and particulate removal; additional improvements to further increase lead and particulate removal, and to enhance retrofitability are planned.

EPI 000241

II. INTRODUCTION

In the United States, 200,000 tons of lead and one million tons of particulate matter are spewed into the atmosphere each year.[1] Motor vehicles are responsible for essentially all of the lead and up to 10% of the particulates. Although at present there is no proof that the amount of lead in urban air is harmful to health,[2,7] lead is poisonous,[8-13] and concern is mounting that long range ill effects may be found.[14,15] In addition, lead is a poison for most catalysts which control carbon monoxide and hydrocarbon emission in exhaust.[16,17] Therefore, control of automotive lead emissions will probably occur within the next few years.[18,19]

A. CONTROL OF LEAD IN AUTOMOTIVE EXHAUST

There are two ways to control lead emitting from automobile exhausts. One can either remove the lead from the exhaust after combustion or prohibit its addition to gasoline as antiknock lead tetraethyl or lead tetramethyl.[20] The present trend is to prohibit its use in gasoline.[21,22] However, this could open a Pandora's box to new problems according to Ethyl Corporation[23] – one of the largest suppliers of lead antiknock additives. Lead removal from gasoline would increase the price from 1 to 6¢/gal,[24-27] if present octane ratings are maintained. Removal of lead may cause valve problems,[2,23] consume more petroleum reserves,[23,28] throw the lead and chemical industry into an economic upheaval,[2,29-31] and may cause other problems.[23,32]

It was found at Atomics International that lead compounds can be effectively removed from automobile exhaust by scrubbing the exhaust with molten alkali carbonate eutectic.[33] This technique of controlling lead emission has the advantage that the exhaust is kept hot for further catalytic treatment to control nitrogen oxides, hydrocarbon and carbon monoxide emission and it simultaneously removes sulfur oxides,[34] particulate matter [33] (which are both known catalyst poisons), and partially removes nitrogen oxides.[33]

B. NATURE OF LEAD IN AUTOMOTIVE EXHAUST

Antiknock tetraethyl lead (TEL) is added to gasoline to improve the octane rating; ~1 gm/gal will improve gasoline antiknock properties three octane

EPI 000242

numbers;[20] additional amounts of TEL are less effective in increasing the octane rating. A maximum of ~3 to 3.5 gm/gal of TEL is added to gasoline feedstock to improve the octane rating ~8 octane numbers.[2,20] Alkyl chloride and bromide are also added to gasoline to keep lead deposits from building up in the engine.[20] Volatile lead halides are the main lead compounds in exhaust. Approximately 60 to 80% of the lead in the gasoline is found in the exhaust;[35,36] most of the rest of the lead is found in the oil drained from the crankcase. Studies have shown that lead concentration in the exhaust is strongly dependent upon the operating mode of the automobile.[36] At slow speeds much of the lead builds up in the engine and exhaust system; the buildup is removed from the system during high speed (high temperature) operation of the automobile.[36] Therefore, lead concentrations in the exhaust vary from nil to as high as 500 $\mu g/\ell$; under normal driving speeds the lead concentration in the exhaust is from 1 to 40 $\mu g/\ell$. (See References 35 through 37.) The lead concentration in ambient urban air is three to four orders of magnitude less or 10^{-2} to 10^{-3} $\mu g/\ell$.[38-43]

1. Concentration of Lead Chloride in Gaseous Mixtures

The vapor pressure of lead chloride, both liquid and solid (mp 501 °C), has been measured by several investigators[43-48] and summarized in two readily available references.[49,50] The data for the vapor pressure of the liquid are in agreement[43] while the reported vapor pressure of the solid are in poor agreement. Furthermore, the vapor pressure at the melting point, calculated from the equation for the vapor pressure of the solid,[50] does not correspond to the liquid vapor pressure at the melting point; therefore, it is believed that the solid vapor pressure is in error. Consequently, in Figure 1 where the lead chloride vapor pressure is given, the solid vapor pressure is dotted and drawn so that at the melting point the vapor pressure of solid and liquid are identical. Using the ideal gas law, the maximum concentration of gaseous lead chloride as a function of temperature has been calculated from these vapor pressures from Figure 1. Figure 2 shows the equilibrium concentration of lead chloride in equilibrium with both liquid and solid lead chloride as a function of temperature. Again, the curve for the solid is dotted to reflect the uncertainty in the data. These data show that at 400, 450, and 500 °C the maximum concentration of gaseous lead chloride in equilibrium with the solid is 12, 170, and 1200 μg Pb/ℓ, respectively. At 500, 550, and 600 °C, the maximum concentration of

EPI 000243

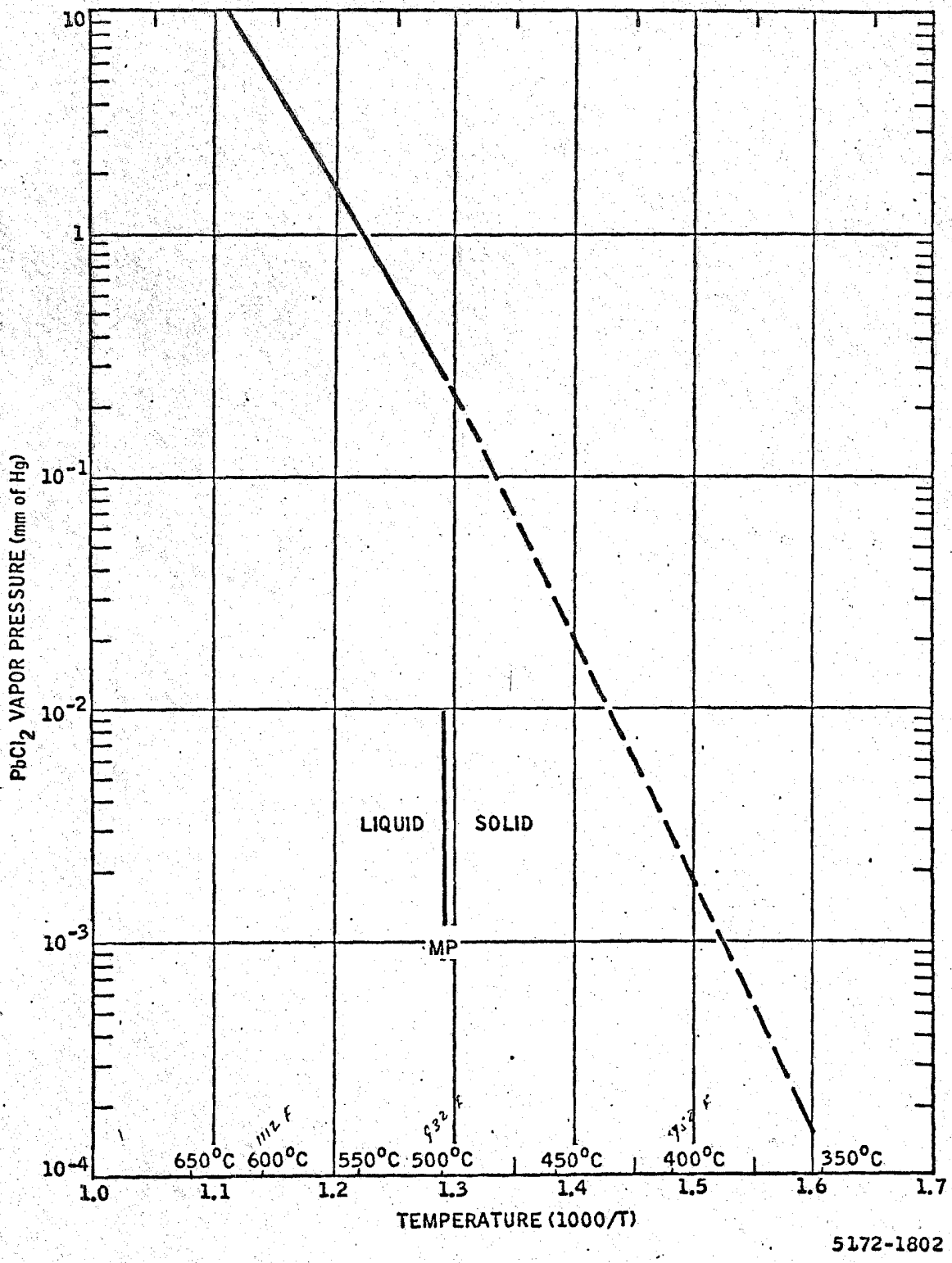


Figure 1. Vapor Pressure of Lead Chloride

EPI 000244

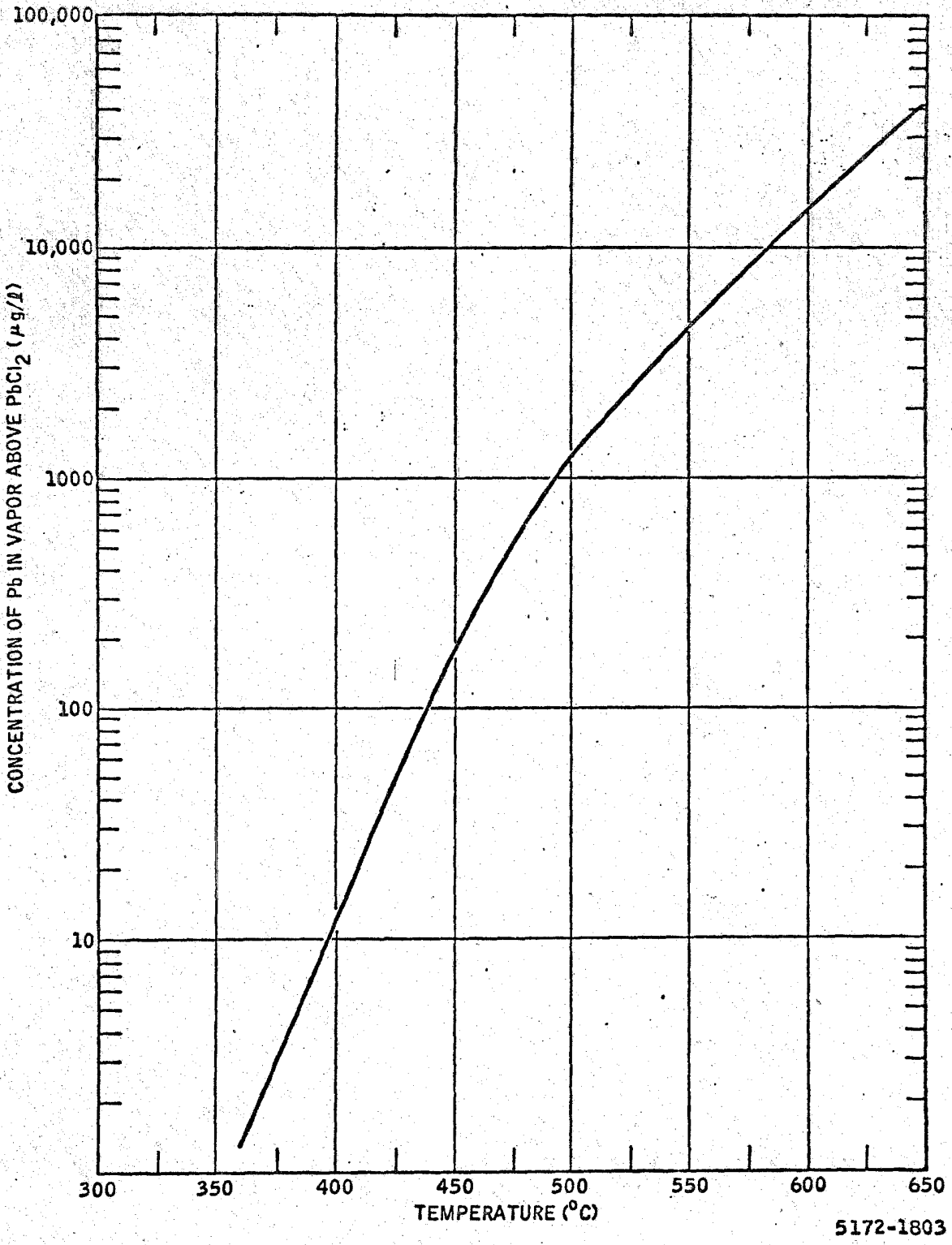


Figure 2. Concentration of Lead in Vapor Above $PbCl_2$ as a Function of Temperature

EPI 000245

gaseous lead chloride in the vapor state in equilibrium with the liquid is ~1200, 4600, and 15,000 μg Pb/ℓ, respectively.

2. Size of Lead Particulates in Automotive Exhaust

The Swiss Commission,[51] using an electron microscopic technique, reports the size of lead particulates in automotive exhaust as between 2 and 100 mμ (millimicrons). However, several workers[37,52-57] have found that mass median diameter of lead particulates in urban air is considerably larger, i.e., between 200 and 600 mμ. Further work will be required to establish the size distribution and factors which influence the size distribution. Since initially the lead compound was present in the gaseous state, the particulate size observed may have depended on the sampling procedure.

C. THE MOLTEN CARBONATE METHOD TO CONTROL PARTICULATES IN AUTOMOTIVE EXHAUST

Lead halides are mildly acidic substances, therefore they would be expected to react chemically with basic alkali metal carbonate eutectic. This is the basis for the use of molten alkali metal carbonate eutectic to scrub gaseous, liquid, or solid lead halides from automotive exhaust.[33] Since molten alkali metal carbonate eutectic[58] is a stable nonvolatile, nonviscous liquid above its melting point (397°C), it can readily be brought into contact with automotive exhaust in a molten salt scrubber. The alkali carbonate eutectic has a moderate surface tension (e.g., 236 dynes/cm at 455°C); therefore, it will wet particulate matter and subsequently remove them from the gas stream. The alkali carbonate eutectic has been studied extensively as a fuel cell electrolyte and as an absorbent for sulfur dioxide[34,59] under contract PH 28-67-128.[60] Consequently many of its physical, chemical, and corrosion properties are known. These are given in Appendix 1.

In an automotive molten carbonate scrubber, the heat of the exhaust is used to melt the salt and maintain it in a molten condition. The exhaust temperature as a function of the distance from the manifold flange at various speeds[61] is given in Figure 3. These data show that except at idle the exhaust is hot enough to melt the salt and maintain it in a molten state. At temperatures above 650°C, corrosion may be a problem; therefore some means of cooling the exhaust may

EPI 000246

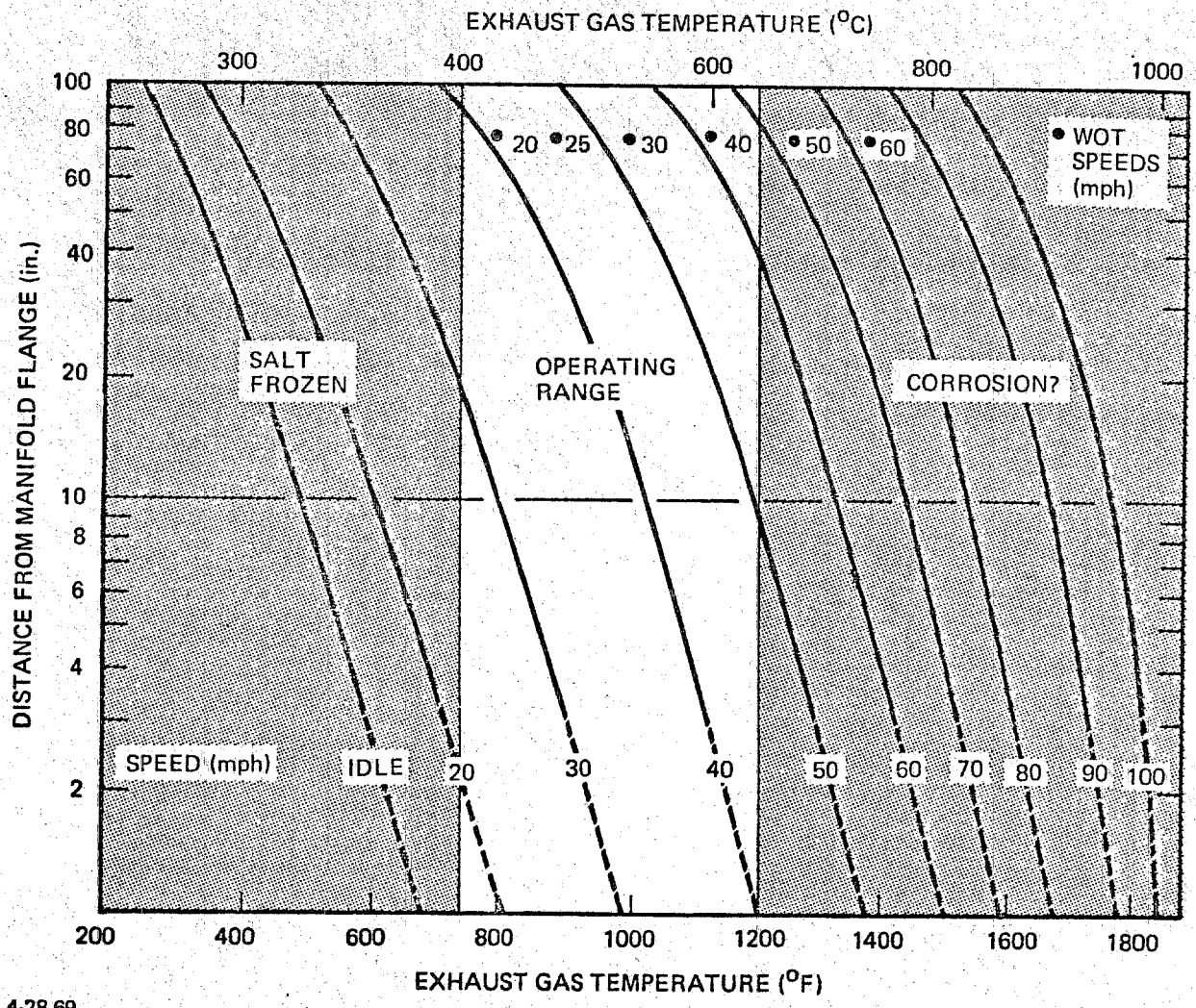


Figure 3. Exhaust Temperature vs Distance From the Manifold Flange(61)

EPI 000247

be desirable. The data in Figure 3 show that this can readily be accomplished by allowing a portion of the exhaust gas to cool in a longer exhaust pipe prior to contacting the molten carbonate.

In addition to the exhaust temperature,[61] the large variation in the exhaust flow rate[62] at different speeds must be considered. The approximate exhaust temperature, 30 cm (1 ft) from the manifold flange and the flow rate of exhaust at 20, 40, and 60 mph and at wide open throttle (WOT), are given in Table I. (Unless stated otherwise, all flows in this report are expressed in actual volumes, not standard volumes.) From these exhaust temperatures and flow rates, other exhaust parameters related to a molten carbonate smog device have been calculated; these are given in Table I. The exhaust velocity was calculated for the various flows passing through a 0.046 m^2 (1/2-ft^2) area; the impingement velocity is the velocity of gas exiting from a 5-cm (2-in.) pipe. The residence time of the exhaust gas in a 0.014 m^3 (1/2-ft^3) device is reported in Table I. Lead concentrations are estimates only; at 60 mph, it was assumed that all the lead in the gasoline containing 3 gm/gal is exhausted. In addition to the calculated exhaust variables, the range over which those parameters were varied in these laboratory scrubbing tests is also given in Table I.

EPI 000248

TABLE I

APPROXIMATE VALUES OF AUTOMOTIVE EXHAUST VARIABLES

Variable	Conditions	Cruising Speed (mph)				Ranges Studied
		20	40	60	WOT*	
Exhaust Temperature (°C)	30 cm (1 ft) from manifold†	350	500	700	900	355 to 600
Exhaust Flow (scfm)	average§	20	40	65	200	-
Exhaust Flow (actual ℓ/sec)	average	20	50	100	365	-
Velocity (m/sec)	0.046 m^2 (0.5-ft^2) surface	0.4	1	2	8	0.5 to 1.9
Impingement Velocity (m/sec)	5-cm (2-in.) pipe	12	30	70	190	12 to 98
Residence Time (sec)	0.014 m^2 (0.5-ft^3) device	0.7	0.3	0.1	0.04	0.01 to 0.1
Lead Concentration ($\mu g/\ell$)	approximate average	1	10	30	500	25 to 300

*Wide Open Throttle
†Reference 61
§Reference 62

EPI 000249

III. EXPERIMENTAL APPARATUS

The apparatus used in the laboratory experiments consisted of a lead particulate generator, a molten salt scrubber, and several post-scrubber traps. The particulate generator and the wetted-wall, wetted-mesh and impingement molten salt scrubbers are discussed below.

A. THE PARTICULATE GENERATOR

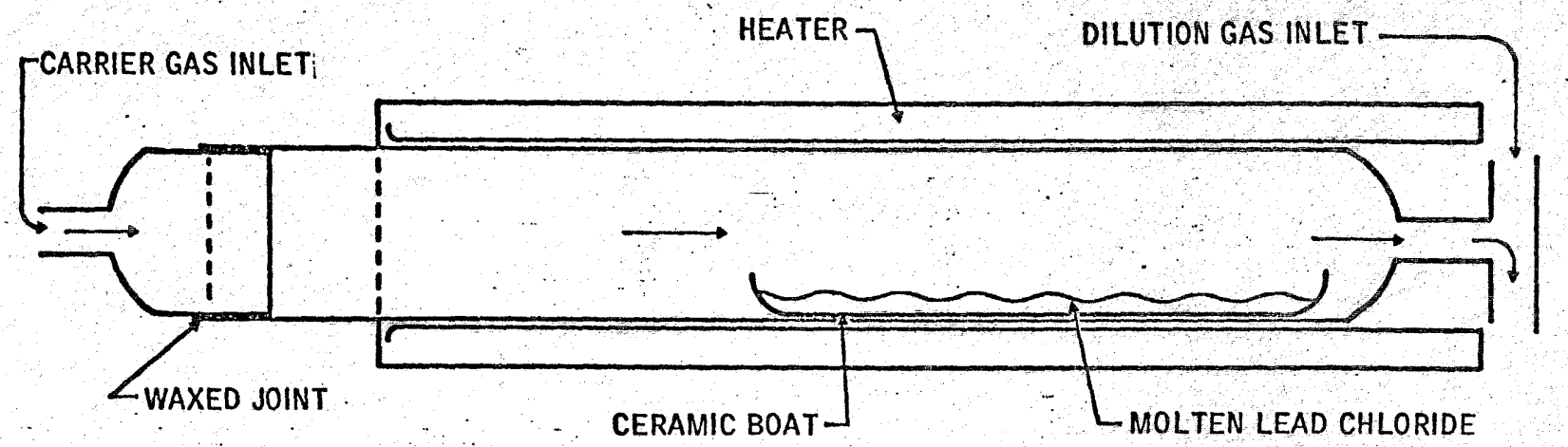
Lead halide particulates were generated in a device shown in Figure 4. This consisted of a ceramic boat full of molten lead chloride inside a heated metal tube; a carrier gas was slowly passed through this tube to carry the lead chloride vapor from the generator into a dilution gas. The molten lead chloride was maintained at a temperature of ~575 to 600°C. The carrier gas flow rate varied from 30 to 300 standard cc/min as the dilution gas flow varied from 3 to 21 standard liters/min. Lead chloride particulate concentrations of 25 to 370 μg/actual liter were obtained in the molten salt scrubbers.

B. COCURRENT WETTED-WALL SCRUBBER SYSTEM

The apparatus used in the cocurrent scrubber tests is shown in Figure 5. In this system a N_2 pump gas was used to pump the melt up from the reservoir so that it would flow down through the wetted-wall contactor. The post-scrubber traps consisted of an ice-cooled condenser, an aqueous sodium hydroxide trap, and aqueous nitric acid trap. In some tests, a second molten carbonate bubble-through, wetted-mesh scrubber was inserted between the molten salt scrubber and the ice-cooled condenser. An in-line, wet-test meter following the post-scrubber traps was used to measure the gas flow rate.

The cocurrent scrubber is shown in more detail in Figure 6. The molten salt pump gas feeds down through the center tube forces melt up to the wetted-wall columns where it contacts the gas-containing particulates. The melt and gas containing particulates flow cocurrently down the wetted-wall columns to the melt reservoir where the gas reverses direction and the melt globules return to the reservoir.

EPI 000250



AI-70-47
16

Figure 4. Lead Particulate Generator

EPI 000251

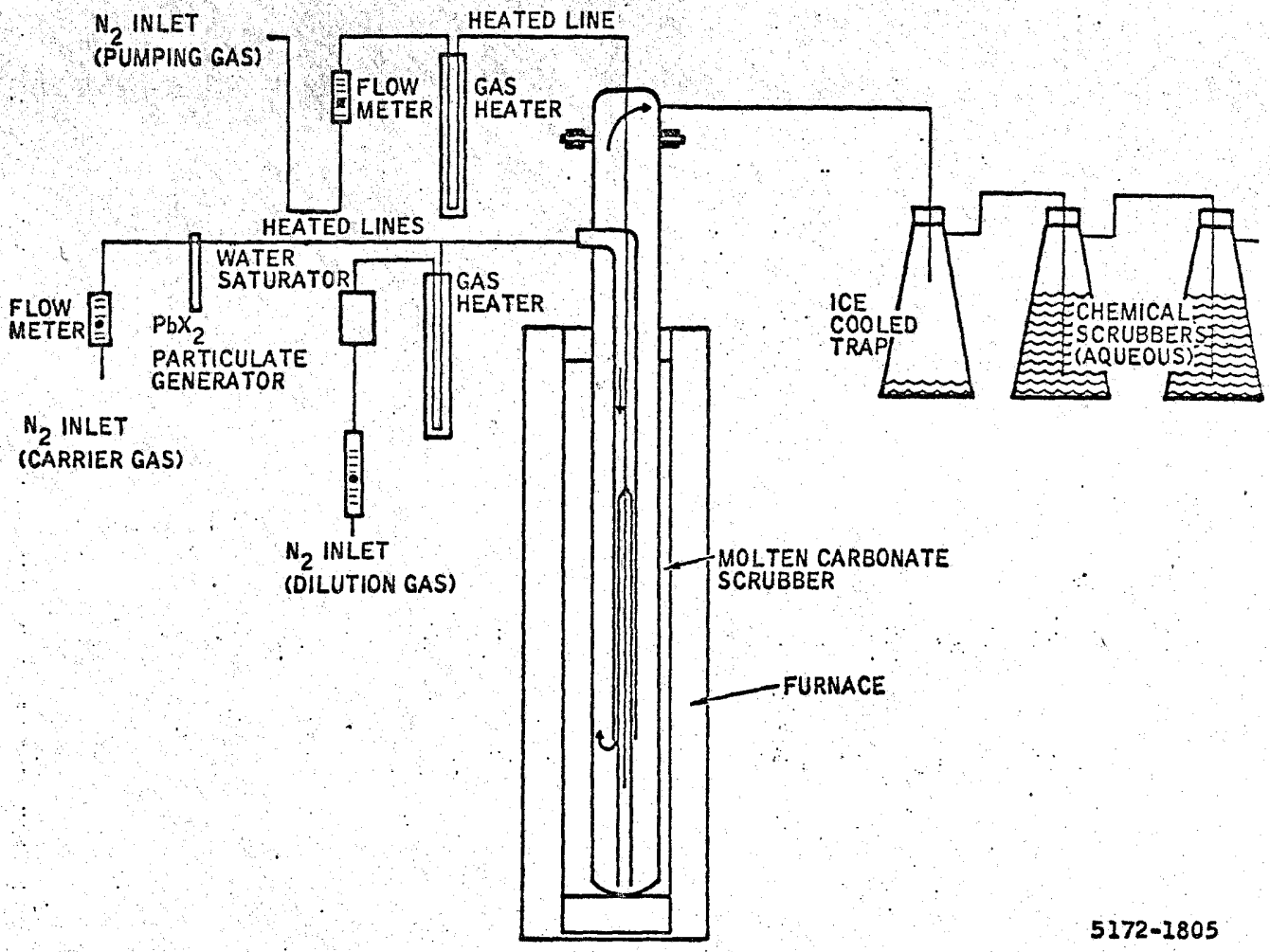


Figure 5. Cocurrent Wetted-Wall Test System

EPI 000252

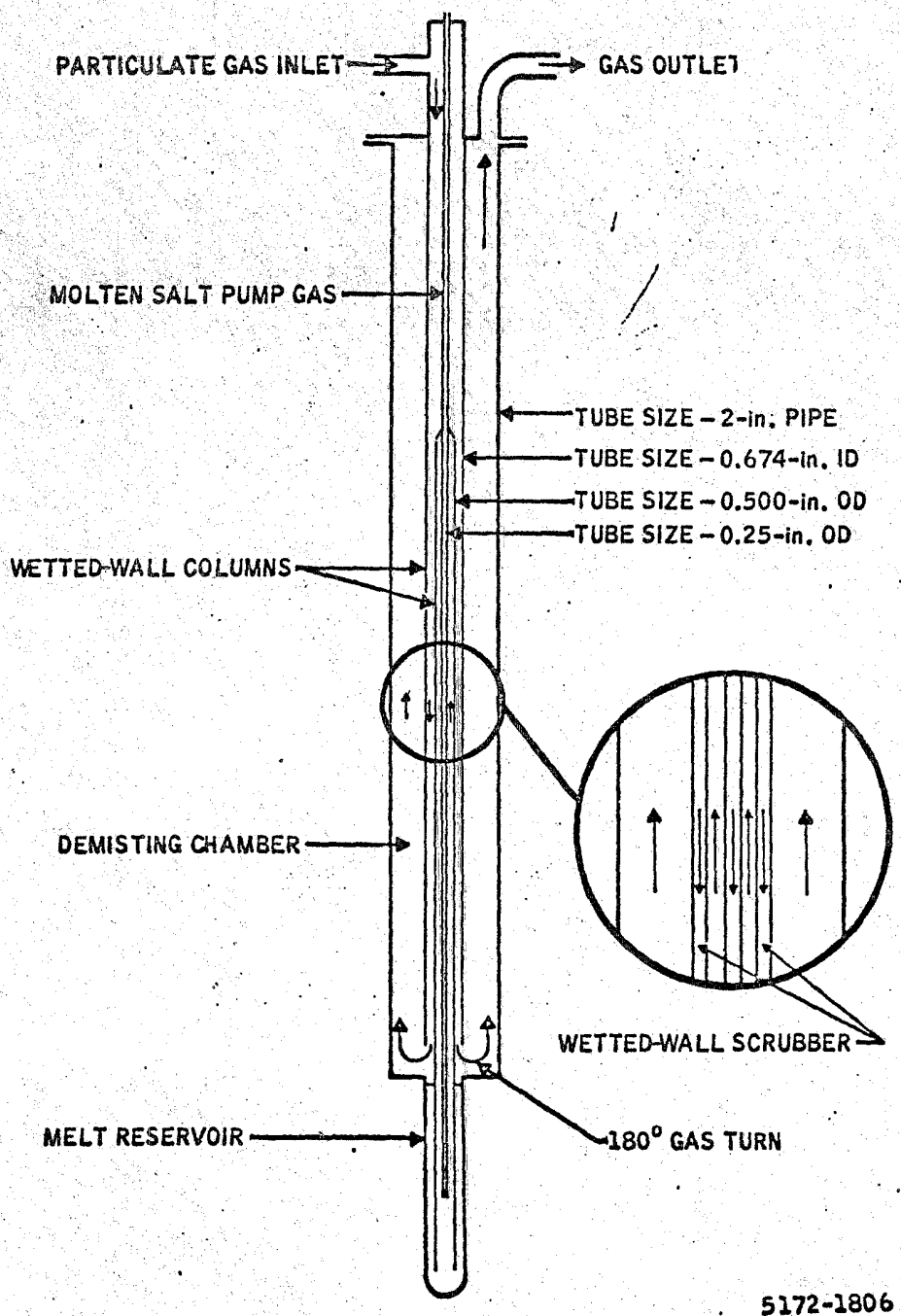


Figure 6. Cocurrent Scrubber

EPI 000253

C. WETTED-MESH SCRUBBER

The molten carbonate wetted-mesh scrubber is shown in Figure 7. It consisted of a 1-in. ID stainless steel tube 18 in. long. The inlet for the gas (containing lead particulates) was at the side of the tube ~1/2 in. above the molten carbonate level in the tube. The gas containing lead particulates passed up through a section (in some cases two sections) of stainless steel wetted-mesh. The lower section of wetted-mesh was 1-1/4-in. thick and was constantly wetted with molten carbonate which was pumped up from the molten salt reservoir by a pump gas bubbling up through the melt pump tube. In some cases, a second section of mesh was included above the lower section. The second section of mesh was wetted by carbonate entrained in the gas when it passed through the lower sections of mesh. The second section of mesh varied in thickness from 0 to 5-1/4 in.; only the portion of the mesh that was wetted during the experiment was considered in calculating the gas residence time in the wetted-mesh reactor. Different thicknesses of mesh were used in order to vary the gas residence time in the mesh without varying the gas velocity through the mesh.

D. IMPINGEMENT – WETTED-MESH SCRUBBER

In order to determine the fraction of the lead chloride removed by impingement and by wetted-mesh, a combination scrubber in which both mechanisms of lead removal occurred was used. A diagram of this combination scrubber is given in Figure 8. The dilution gas (nitrogen staurated with water vapor at 50°C) inlet is at the top of the figure; the carrier gas containing the lead chloride vapor is fed into the dilution gas at this point. The gas stream passed down through a 3/8-in. OD tube where it impinged against a molten salt surface. The gas then passed up through four separate sections of Type 304 stainless steel mesh that had been prewetted (dipped in molten alkali carbonate and allowed to drain overnight at 500°C). Four separate sections of mesh were used to determine if all sections of the wetted-mesh were equally effective in removing particulates. The volume occupied by each mesh section was 0.675 $in.^3$. Each mesh section had a metal surface area of 13.1 $in.^2$ and metal packing density of 2.92 $gm/in.^3$. Approximately 2 to 3 gm of melt were retained on each mesh section.

EPI 000254

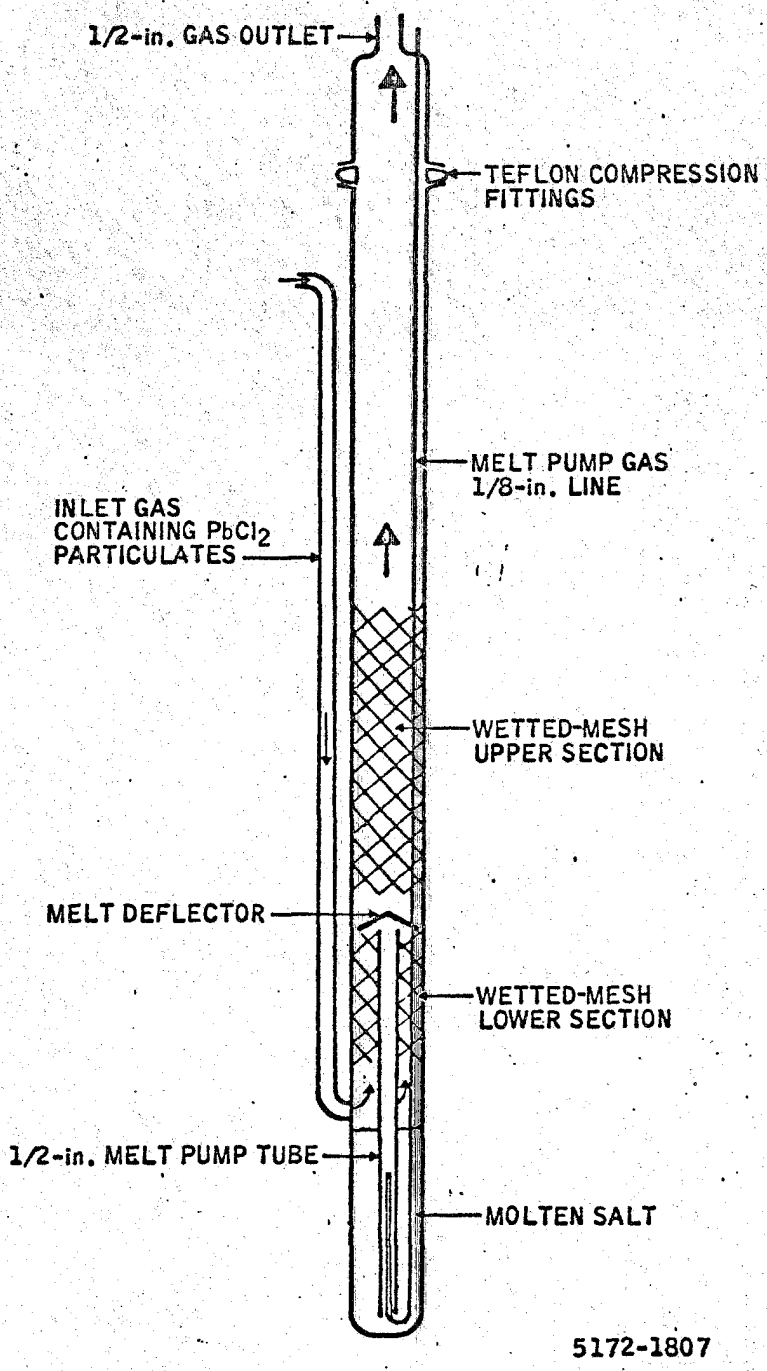


Figure 7. Wetted-Mesh Scrubber

EPI 000255

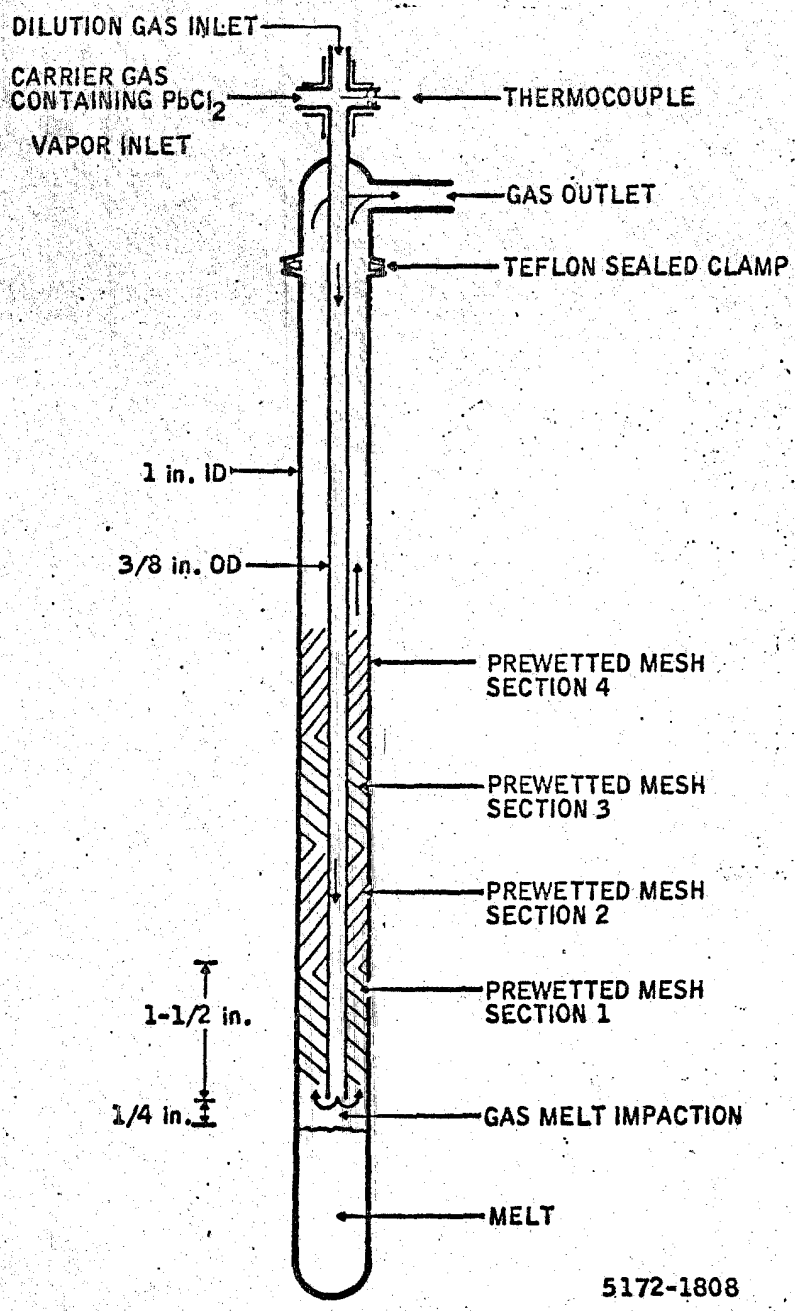


Figure 8. Impingement – Prewetted-Mesh Scrubber

EPI 000256

E. AUTOMOTIVE EXHAUST SCRUBBER

The exhaust was sampled before and after the lead removal device by drawing gas samples through 0.45 μ millipore filters followed by aqueous scrubbers. The dual sampling system sampled the inlet and outlet exhaust streams simultaneously. After 500 to 1000-liter gas samples were drawn through the sampling systems, the particulates were washed from the sampling system into a large beaker where the water was slowly evaporated at 60°C. After the residue was dried to constant weight, a benzene extraction and a water extraction of the particulate residue was made to determine the fraction of organic and inorganic materials present.

EPI 000257

IV. TEST PROCEDURE

A typical experimental test system is shown in Figure 5; the various scrubbers described were substituted for the cocurrent wetted-wall scrubber shown in Figure 5. Approximately 5 to 6 gm of $PbCl_2$ were placed in the boat in the partuclate generator and ~100 gm of alkali metal carbonate eutectic were placed in the scrubber. The post-scrubber traps were filled with aqueous solution or molten salt. The test system was assembled and brought up to the desired temperature. The carrier gas flow was started through the particulate generator and the dilution gas flow was started through the preheater. (A molten carbonate or a coiled copper or stainless steel preheater was used in these tests.) The tests were 1 to 3 hr in duration.

Since gaseous, liquid and solid lead chloride were used in the tests, simple gas sampling before and after the scrubber could not be used to determine the particulate removal efficiency. In preliminary attempts to use this technique to determine lead removal efficiency, more than half of the lead condensed out on the walls of the sampling system; furthermore, the amount of lead that condensed out on the sampling system wall was not reproducible. Therefore, the test assembly was dismantled and boiled in nitric acid to remove the lead from the entire system. These various solutions were analyzed for lead by atomic absorption spectroscopy. In general, 95+% lead material balances were obtained in the tests. Tests showed that the remainder of the lead had penetrated the wall of the lead particulate generator and could be removed only by dissolving the inner layers of the metallic particulate generator in strong acid. The lead particulate removal efficiency was calculated from the amount of lead in the molten salt scrubber divided by the total amount of lead found in the molten salt scrubber and the post-scrubber traps.

EPI 000258

V. RESULTS AND DISCUSSION

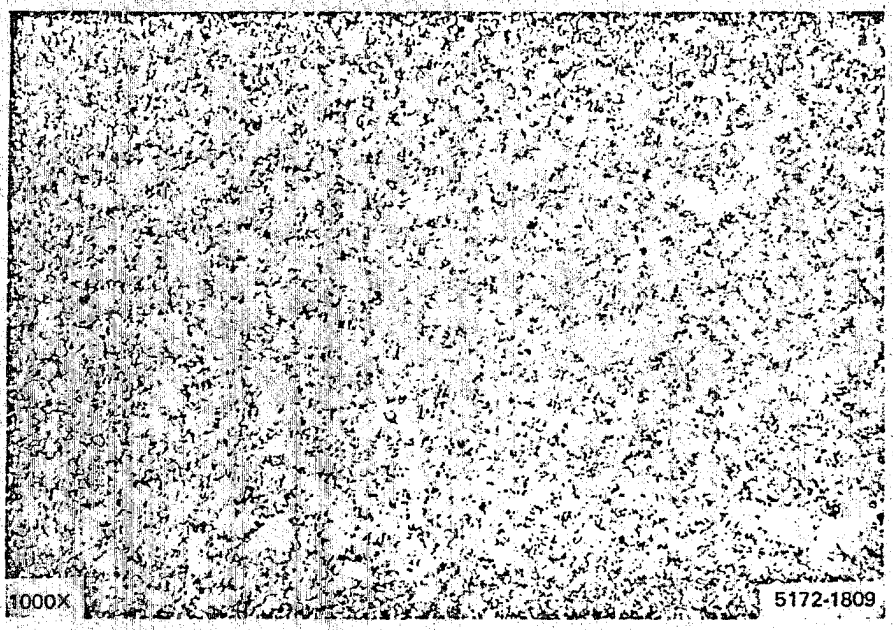
A. SIZE OF PARTICULATES CONDENSED FROM THE GENERATOR

Particulates were filtered from side gas streams of the inlet and outlet to the molten salt scrubbers with 0.45μ and 0.1μ millipore filters. In general, only a few milligrams of lead chloride were collected on the filter. These particulates were examined microscopically to determine the particulate size.

Thousand-fold magnification (1000X) photographs of lead particulates filtered from the gas streams used in our test system are given in Figure 9. Figure 9a shows the particulate size of lead chloride particulates filtered from a gas stream containing 500 $\mu g/\ell$ of lead chloride; this is somewhat higher than the maximum concentration of lead particulates used in our particulate removal experiments (370 $\mu g/\ell$). These particulates were filtered from the gas stream after the gas had passed through the scrubber in a test in which no melt was in the scrubber. The concentration of particulates on the VC Millipore filter was approximately 1000 μg of $PbCl_2/cm^2$. The particulates appear to be one micron or less in size with an oblong rather than a spherical shape. Figure 9b shows the particulate size of lead chloride particulates filtered from a gas stream containing about 10,000 μg of $PbCl_2/\ell$. This is about the concentration of $PbCl_2$ in the particulate generator before it is diluted by the dilution gas. The particles shown in Figure 9b were filtered from the particulate generator carrier gas after the gas containing particulates was maintained at 600°C for several seconds. Under these conditions the particles tend to agglomerate into spherical particles as large as three microns in size. These results show that in order to simulate the size of lead particulates found in automotive exhaust it is important to dilute the carrier gas stream containing particulates in order to prevent growth or agglomeration of the lead halide particulates when the gas stream is cooled. Therefore, the gas was diluted ~30 fold in our particulate removal experiments.

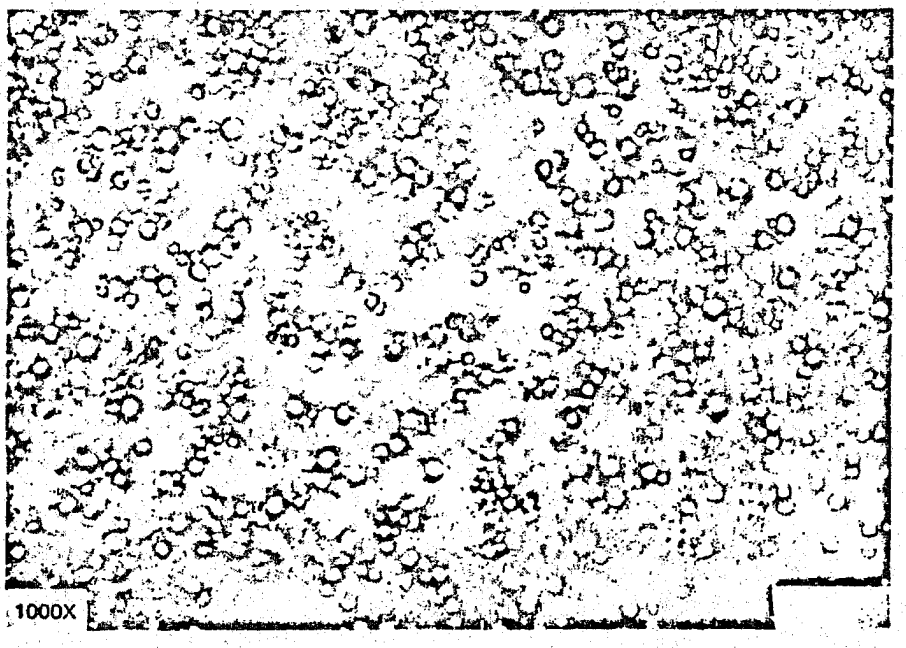
Attempts were made to use an electron microscope to observe the size of lead halide particulates. Whenever the electron beam was focused on the particulates on the millipore filter, the lead halide particles "evaporated" or "deagglomerated" into very fine particles of ~10 mμ size. Thus the use of an electron microscope to obtain the size distribution of lead halide particles

EPI 000259



(Particulate concentration in gas stream was 500 μg $PbCl_2/\ell$.)

Figure 9a. Photomicrograph of Lead Chloride Particulates on a 100 mμ millipore Filter Containing ~1000 μg $PbCl_2/cm^2$



(Particulate concentration in gas stream was 10,000 $\mu g/\ell$.)

Figure 9b. Photomicrograph of Lead Chloride Particulates on a 450 mμ millipore Filter Containing ~15 mg $PbCl_2/cm^2$

EPI 000260

directly was not successful. However, when lead chloride particulates were first removed from the filter paper by ultrasonic dispersion of the particulates in ethyl alcohol in which a standard electron microscopy carbon film was dipped, small lead particulates were revealed in an electron microscope. In contrast to previous results, lead chloride particulates prepared on microscope slides in this manner did not "vaporize or deagglomerate" when the electron beam was focused on them. As shown in Figure 10, the particulates were long strings up to 2μ in length and less than 0.1μ in diameter. These strings were composed of numerous (20 to 30) particles which were 0.1 to less than 0.01μ in size.

The results show that an electron microscopic technique might perhaps be used to determine lead halide particulate size; however, further study must be made to determine if the particulates observed in the electron beam are the same as the original particulates collected. The particulates discussed above were somewhat similar to, but definitely composed of smaller diameter chains than those shown in Figure 9a. Thus it would appear (as might be expected) that the method used above did modify the nature of the particulate chains. However, it would also appear that the particulate generator produces very small particulates, 0.01 to 0.1μ in size, that tend to agglomerate in chains prior to the formation of the larger spherical particulates shown in Figure 9b.

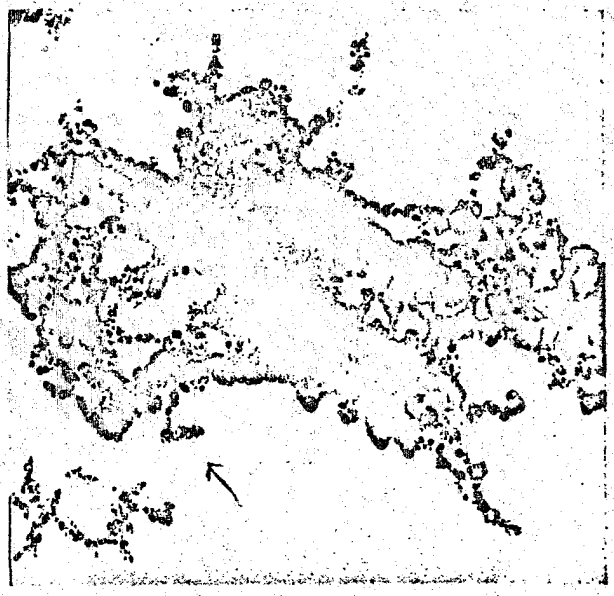
B. LEAD REMOVAL EFFICIENCY

1. Wetted-Wall Scrubber

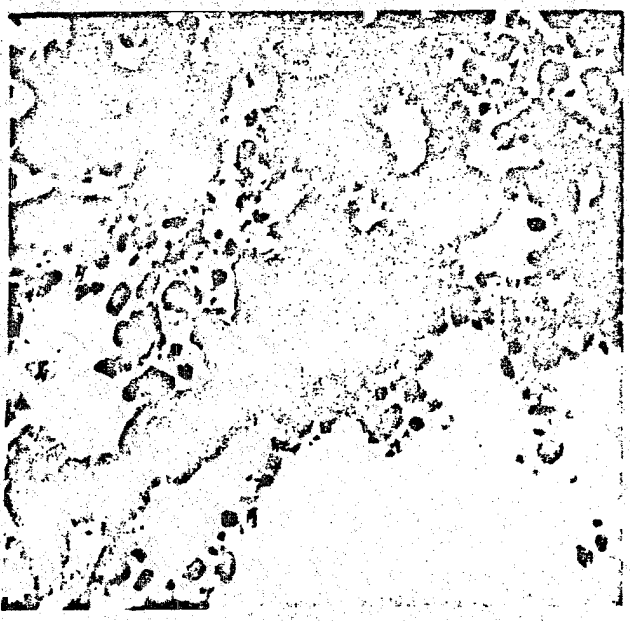
The lead removal efficiency of the wetted-wall scrubber (Figure 6) and the lead material balance is given in Table II. The lead removal efficiencies given in parenthesis are the efficiencies if all of the missing lead passed through the scrubbers; however, subsequent tests proved that the missing lead was in the generator. In this series, a test with no melt in the scrubber (Test 1, Table II), a test with melt only in the reservoir (Test 2), and two tests with melt in the reservoir and in the wetted-wall column (Tests 3 and 4) were run. Even without melt in the reservoir, some of the lead (28%) was trapped in the scrubber; this shows that a clean metal surface removes a portion of lead chloride at these temperatures. With melt only in the reservoir and not in the wetted-wall, 89 to 98% of the lead was removed from the gas phase during scrubbing.

EPI 000261

2500X 5172-1811



20,000X 5172-1812



60,000X 5172-1813

Figure 10.

Electron Micrographs of Lead Chloride Particulates

(Ultrasonically removed from a filter paper and dispersed on a carbon film.)

EPI 000262

TABLE II

LEAD REMOVAL EFFICIENCY OF MOLTEN CARBONATE WETTED-WALL SCR

Test No.	Description	Temperature (°C)		Gas-Melt			Conc Pb ($\mu g/\ell$)	Lead Rem Efficien (%)
		Gas	Melt	Flow Rate (l/sec)	Velocity (M/sec)	Residence Time (sec)		
1	Empty Scrubber	640	530	1.28	12.3	NA	121	28 (14)
2	Molten Carbonate, No wetted column	530	530	1.09	9.2	NA	46	98 (93)
	no pump gas	533	533	0.903	7.6	NA	57	93 (88)
		530	530	0.645	5.2	NA	79	89 (84)
3	Carbonate wetted 24.8 cm column	360	435	0.954	9.1	0.027	25	92 (87)
4	Carbonate wetted 19.7 cm column	630	530	1.12	10.7	0.018	33	99 (71)
		630	530	0.870	8.3	0.024	43	96 (69)
		580	530	0.626	6.0	0.033	58	98 (70)

*Numbers in parenthesis is the lead removal efficiency assuming all lead not recovered the post scrubber traps. Subsequent tests have shown that the missing lead had probabl absorbed into the walls of the lead generator.

EFI 000263

In the tests with wetted-walled columns in addition to impingement of the gas on the melt in the reservoir, 92 to 99% of the lead was removed.

The results of Test 2 show that the lead removal efficiency by impingement of the gas containing lead halides increases as the impingement velocity increases. Test 3 shows that when the gas temperature decreases below the melting point of the salt (397°C), the removal efficiency is less but still quite effective. Test 4 demonstrates the difficulty in establishing trends as a parameter is varied since essentially all of the lead is removed from the gas stream in all three cases.

These results show that impingement of the gas on a molten salt surface is an effective method of removing lead from a gas stream. In fact, impingement is such an effective removal mechanism that it is impossible to determine the wetted-wall removal efficiency in a combination impingement-wetted wall scrubber (Test 4). Since it appeared as if meaningful data would be difficult to obtain in a wetted-wall column, this series of tests was discontinued and wetted-mesh tests were studied.

These results also showed that it was important to determine what had happened to the missing lead. Without accurate removal efficiencies, quantitative design data could not be obtained. Therefore a concerted effort was made to find the missing lead. Additional post-scrubber traps showed that little, if any, of the missing lead was escaping from the system. A test using a closed generator showed that only 90% of the lead could be removed by normal cleaning procedure and that most of the missing lead was absorbed into the wall of the particulate generator. This lead was not removed after each test since this required dissolution of the lead generator.

2. Wetted-Mesh Scrubber

The lead removal efficiency of carbonate wetted-mesh scrubbers is given in Table III. In these tests the velocity, residence time, temperature, and lead concentration in the gas varied independently. From these data the lead removal efficiency as a function of the parameters could be determined. In all cases (except Tests 4 and 7) between 94 and 99% of the lead was removed. Since the lead removal varied over such a small range (<5%), it is difficult to establish definitive trends. Therefore, the lead remaining in the gas stream

EPI 000264

TABLE III

LEAD REMOVAL EFFICIENCY OF A MOLTEN CARBONATE WETTED-MESH SCRUBBER

Test No.	Temperature (°C)		Gas Velocity (m/sec)	Gas Residence Time (sec)	Lead Concentration in Gas ($\mu g/\ell$)	Lead Removal Efficiency (%)	Lead Remaining in Gas (%)
	Melt	Gas					
1	515	550	2.44	0.01	130	94.6	5.4
2	515	540	1.86	0.06	370	97.7	2.3
3	510	500	1.82	0.06	177	98.5	1.5
4	500	550	1.80	0.025	106	92.3	7.7
5	500	500	1.15	0.028	330	94.8	5.2
6	500	430	0.94	0.05	128	94.3	5.7
7	500	355	0.51	0.11	326	82.7	17.3
8	430	500	1.64	0.021	91	98.7	1.3

EPI 000265

(which varies by a factor of 5) is given in Table III and will be discussed below. However, it should be cautioned that a small analytical error can have a large effect on these results since small differences of large numbers are involved. The error in analysis probably introduces an uncertainty of ±0.5% in the reported values, i.e., the lead remaining in the gas stream in Test 1 (Table III) was between 4.9 and 5.9%.

The percent lead particulates remaining in the gas stream appears to increase as temperature of the molten carbonate increases. At a velocity of 1.7 in./sec and a residence time of 0.02 sec, Tests 4 and 8, Table II, the percent lead remaining in the gas stream after contact with the molten carbonate-wetted mesh increased from 1.3 to 7.7% as the mesh temperature was increased from 430 to 500°C. These limited data suggest that as the melt temperature increases, the percent lead particulates remaining in the gas phase after contacting the wetted mesh increases. This is contrary to what one might expect from a kinetics standpoint unless the molten carbonate is more effective in removing particulate than gaseous lead halides and a greater fraction of the lead exists as particulates at the lower temperatures. The data in Figure 2 indicates that particulates should have been present at 430°C (Test 8) but not at 500°C (Test 4). In addition, the technique used to generate the lead may have also allowed particulates to be present. For example, the concentrations of lead in the carrier gas was several times that in the dilution gas or as high as 1800 $\mu g/\ell$ at 575°C in Test 4. When lead carrier gas was cooled to 500°C by the dilution gas, particulates may have formed and not have had time to resublime before the gas contacted the melt. This same sort of phenomenon may exist in automobile exhaust; i.e., lead particulates in a gas that is not saturated with lead halide vapor. Further experimental measurements should be made to show that the lead particulate-vapor ratio obtained in these experiments is the same as in automotive exhaust and that lead removal varies as the particulate to vapor ratio varies.

The fraction of the lead particulates remaining in the gas phase increases as the gas velocity through the mesh increases. At 500°C and a residence time of 0.026 sec (Tests 4 and 5), the percent lead remaining in the gas stream increases from 5.2 to 7.7% as the velocity through the mesh increases from 1.15 to 1.80 m/sec. These data suggest that gas velocity is a critical parameter in device design and probably constrains the design more than demisting.

EPI 000266

The percent lead particulates remaining in the gas stream decreases as the gas residence time in the wetted mesh increases (Tests 2, 3, and 4). At a temperature of 500°C and a gas velocity of 1.8 m/sec, the percent of the lead remaining in the gas stream decreases from 7.7% to less than 2% as the residence time is increased from 0.025 to 0.06 sec. Since gas residence times of one-tenth of a second can probably be obtained in an operating device (even at wide open throttle), residence time will probably not be as critical a parameter as gas velocity in the device design.

Within the limits of experimental error it does not appear that the percent lead remaining in the gas phase after contact with the scrubber is a function of lead concentration in the gas phase. At velocities of 1.8 m/sec and residence time of 0.06 sec (Tests 2 and 3), the lead remaining in the gas phase was ~2% when the lead concentration decreased from 370 to 177 $\mu g/\ell$.

An attempt was made to duplicate conditions in an operating device as an automobile idled at a stop light. The temperature of the gas containing the lead particulates was 355°C, i.e., below the melting point of the molten carbonate. Therefore, the melt on the wetted-mesh scrubber was probably cooled below its freezing point (397°C); only the melt being pumped over the mesh was molten (temperature 500°C). In this test, the gas residence time (0.11 sec) was much shorter than might be expected under idle conditions (~1 sec), and the gas velocity (0.5 m/sec) was approximately that which might be expected in an automobile device. Even under these conditions, only 17% of the lead remained in the gas stream. An order of magnitude increase in gas residence time, as might be expected in an operating device, would probably decrease the lead remaining to a negligible amount. Therefore, at idle, essentially all of the lead particulates will probably be removed.

3. Impingement Scrubber

The lead removal efficiency by impinging the gas on a molten carbonate surface is given in Table IV. At the conclusion of each scrubber test, the amount of lead in the melt and on each section of the mesh was determined. At a gas temperature of 600°C, gas impingement velocities of 34 and 5 m/sec on the 500°C melt surface resulted in removal of 76 and 12% of the lead, respectively (Runs 4 and 5). In Tests 1, 2, and 3 at a gas temperature of 530°C, the

EPI 000267

TABLE IV

LEAD REMOVAL EFFICIENCY IN THE COMBINATION IMPINGEMENT – WETTED-MESH SCRUBBER

Test No.	Temperature (°C)			Gas Velocity (m/sec)		Time in Mesh (sec)	Gas Conc. of Pb ($\mu g/\ell$)	Lead Removal (%)					
								By Impingement	Mesh Section				
	Gas	Mesh	Melt	Impingement*	Mesh				1	2	3	4	Total
1	530	NA	530	9.2	NA	NA	46	97.7	NA	NA	NA	NA	97.7
2	533	NA	533	7.6	NA	NA	57	92.5	NA	NA	NA	NA	92.5
3	530	NA	530	5.2	NA	NA	79	89.0	NA	NA	NA	NA	89.0
4	600	500	505	33.6	2.43	0.071	43	75.6	16.0	7.4	0.2	0.2	99.4
5	600	500	505	4.9	0.35	0.48	59	12.2	53.6	30.1	0.5	0.4	96.8

*Impingement velocity in automobile at 200 scfm (wide open throttle) through 2-in. pipe is ~190 m/sec (~600 ft/sec); at 4 scfm (40 mph) the impingement velocity is ~30 m/sec (~100 ft/sec).

NA – Not applicable since wetted mesh was not included in these tests.

EPI 000268

removal efficiency dropped similarly from 98 to 89% as the impingement velocity dropped from 9.2 to 5.2 m/sec. Thus at constant temperatures the amount of lead removed by impingement increased as the velocity increased. As shown in Table IV, impingement appears to be more effective as a removal process at lower gas gemperatures (Tests 3 and 5); this same temperature effect was observed in the wetted-mesh scrubbers (Tests 4 and 8, Table III). This temperature effect is not clearly understood but is probably related to the particulate-vapor ratio of lead in the gas stream (see discussion given previously).

At wide open throttle in an automobile (200 scfm), impingement velocities from a 2-in. pipe would be approximately 190 m/sec (600 ft/sec). At this velocity these data suggest that essentially all of the lead particulates would be removed by impingement alone. At a gas flow of 40 scfm (40 mph) the impingement velocity would be approximately 30 m/sec (100 ft/sec). Under these conditions of flow and temperature (Table I), essentially all of the particulates will be removed by impingement. Thus impingement velocity is a very significant design parameter. Due to removal by impingement at high velocities, a significantly more compact device can be used than if contact with wetted mesh were the only particulate removal mechanism.

The percent of the lead particulates removed by each mesh section compared to the total amount of lead found in the scrubber and in each post-scrubber trap is shown in Table IV, Tests 4 and 5. The percent of lead retained by each mesh section decreases from Sections 1 to 4.

Another way of representing the lead removal efficiency of eash mesh section is to determine the portion of the lead removed in each section compared to the amount of lead remaining in the carrier gas at the time it contacts the mesh section. The results are shown in Table V. These data show that Mesh Section 2 was much more efficient than the other mesh sections and that Mesh Sections 3 and 4 were only about 1/4 as efficient as Mesh Section 2. Since the residence time, and gas velocity were the same for each mesh section, this shows that some other parameters such as packing density, surface area, melt content on the mesh, or particulate-vapor ratio of lead are influencing the removal. These factors as well as the temperature effect discussed above should be identified.

EPI 000269

TABLE V

FRACTION OF THE LEAD RETAINED ON EACH WETTED-MESH SECTION. COMPARED TO THE AMOUNT OF LEAD REACHING THE MESH SECTION

	Lead Retained/Total Contacting Mesh Sections (mg)				Lead Removal Efficiency of Each Mesh Section (%)			
Test No.*	1	2	3	4	1	2	3	4
4	67.4/102.4	31.0/35.0	0.76/4.01	0.65/3.25	66	89	19	20
5	45.6/74.7	25.6/29.1	0.45/3.53	0.33/3.08	61	88	13	11

*Same as Tests 4 and 5 in Table IV, respectively.

4. Automotive Exhaust Molten Salt Scrubber

The Automotive Exhaust Molten Salt Scrubber was tested under two driving cycles. The first driving cycle was start and stop surface street driving where the maximum speed was 30 to 40 mph. The second driving cycle was a 10-mile stretch of a freeway where the maximum speed was 70 mph. (Since this section of the freeway is over a mountain pass, nearly wide open throttle could be maintained for over one minute.)

The data in Table VI show that 66 and 74% of the total particulates are removed by the device under the slow and fast driving tests, respectively. A variable fraction (20 to 50%) of the particulates collected were soluble in benzene, i.e., were organic in nature. These data showed that 19 and 38% of the organic particulates were removed by the molten carbonate device operating under the two driving cycles. Since the removal efficiency increased with speed (temperature) this probably indicates that a higher percentage of the organic "particulates" were actually particulates at the operating temperature of the device (>400°C). It is not expected that organic materials that are gaseous at ~400°C will be removed by the device. However, these low-boiling organic compounds are readily oxidized catalytically in a post-scrubber catalyst bed. The water soluble materials which are primarily inorganic materials were removed by the molten carbonate device to the extent of about 80%. All of these samples were analyzed for lead; these data indicated that 96 and 84% of the lead

EPI 000270

TABLE VI

PARTICULATE REMOVAL EFFICIENCY OF THE MOLTEN CARBONATE DEVICE ON AN AUTOMOBILE

	Mg in Sample*				Removal Efficiency (%)	
	Inlet		Outlet			
	30-40 MPH	60-70 MPH	30-40 MPH	60-70 MPH	30-40 MPH	60-70 MPH
Total	10.6	44.7	3.6	11.6	66	74
Benzene Extraction	2.6	9.1	2.1	5.6	19	38
Water Extraction	7.7	35†	1.5	6†	81	80
Lead	4.6	21.0	0.2	3.4	96	84

*Normalized to 1000 liter samples

†Obtained by difference, the samples were not at constant weight before lead analysis was performed.

was removed by the molten carbonate scrubber, at 30 to 40 mph and 60 to 70 mph, respectively.

In the automobile exhaust sample taken from the inlet to the molten carbonate device, $PbSO_4$, Pb_2OBr_2, and PbClBr and $Pb(NO_3)_2$ were identified by x-ray diffraction. Other amorphous lead compounds are probably present but could not be identified by this technique. In the automotive exhaust samples taken from the outlet of the automobile device, Pb_2OBr_2 and $PbSO_4$ were identified. Only trace (if any) unidentifiable lead compounds were present in the outlet samples.

Brief tests to determine the nitric oxide removal efficiency of the automobile device were made. In these tests when a catalyst was included in the scrubbing train up to 80% of the nitric oxide could be removed at high speeds; decreased nitric oxide removals were found at lower speeds (lower temperatures). Without the catalyst in the scrubber train, the nitric oxide removal efficiency decreased from 30 to 15% as the speed increased from 30 to 60 mph when the thermactor was connected (excess air in the exhaust) and the removal efficiency decreased from 15 to 5% as the speed increased from 30 to 60 mph when the thermactor was disconnected.

EPI 000271

C. DISCUSSION OF RESULTS

Insufficient data were obtained to test any theoretical relationship between removal efficiency and parameters of interest. Therefore neither graphs of removal efficiency vs parameters nor equations relating the removal efficiency to various parameters are given. The lead removal efficiency in a wetted-mesh scrubber increased as the gas residence time in the wetted mesh increased, decreased as the gas velocity through the mesh increased, increased as the melt temperature decreased and was essentially independent of the lead particulate concentration in the gas stream. The results also indicated that the fraction of lead removed after impingement against a molten salt surface increased as the impingement velocity increased and that removal by impingement is more effective as the temperature decreased.

Since in all cases (except for low-velocity, high-temperature impingement) high lead removal efficiencies were obtained, a conceptual automotive device was designed. Design criteria were established by retrofit requirement, experience with the company-funded automotive molten salt scrubber and by data generated under this contract.

EPI 000272

VI. CONCEPTUAL DESIGN

The conceptual design of a molten salt particulate removal device which is capable of retrofit on Ford Motor Company vehicles is shown in Figure 11. A quarter-scale drawing of this device is given at the end of this report. The gas from the exhaust manifold is brought into the device through the inlet (1).* Approximately 5% of the full throttle flow (12.5ℓ/sec or 0.45 actual ft^3/sec is accelerated through a venturi tube (2), across the venturi throat (3), out the venturi recovery tube (4), and into the reaction zone mesh. It is this venturi action that provides the pumping power to lift the molten salt up through the salt intake tube (6) and disperse the salt into the gas stream. The venturi throat is sized to provide sufficient pressure differential to lift the salt into the venturi throat when the car is operating at approximately 20 mph. The remainder of the exhaust gas (~252ℓ/sec or 9.0 ACFS at full flow) is passed through a bypass valve (7) into the venturi bypass line (8) and is exhausted out through nozzles (9) to impact upon the surface of the molten salt (10). The combined gas stream then passes up through wetted mesh (5) where final removal of particules is accomplished by absorption on the wetted mesh. The absorbed particules are carried with the demisted melt into the melt pool (11) where the heavier particles of lead and corrosion products form a slurry at the bottom of the molten salt pool. After the gases pass through the reaction zone, they flow over a baffle into the demisting zone (12) where final removal of entrained salt is accomplished ACS Industries Inc. mesh style 38F which has a predicted performance of 99.9+% removal of entrained salt is used as the demister. From the demister zone (12), the exhaust gases pass under a baffle and flow up through two baffles (14), make a 90 degree turn, flow down through the exterior jacket (15), past the bottom of the molten salt pool to heat and maintain the salt in the molten salt and out the outlet port (16) to the tail pipe. When servicing is required (approximately every 15,000 miles, see Appendix II), the molten salt is drained from the device through the drain plug (17) and fresh carbonate is added through the fill tube (18).

Within the constraints of limited available space to locate the device and a paucity of design data, the performance of the device was estimated. These

*Numbers shown on Figure 11

EPI 000273

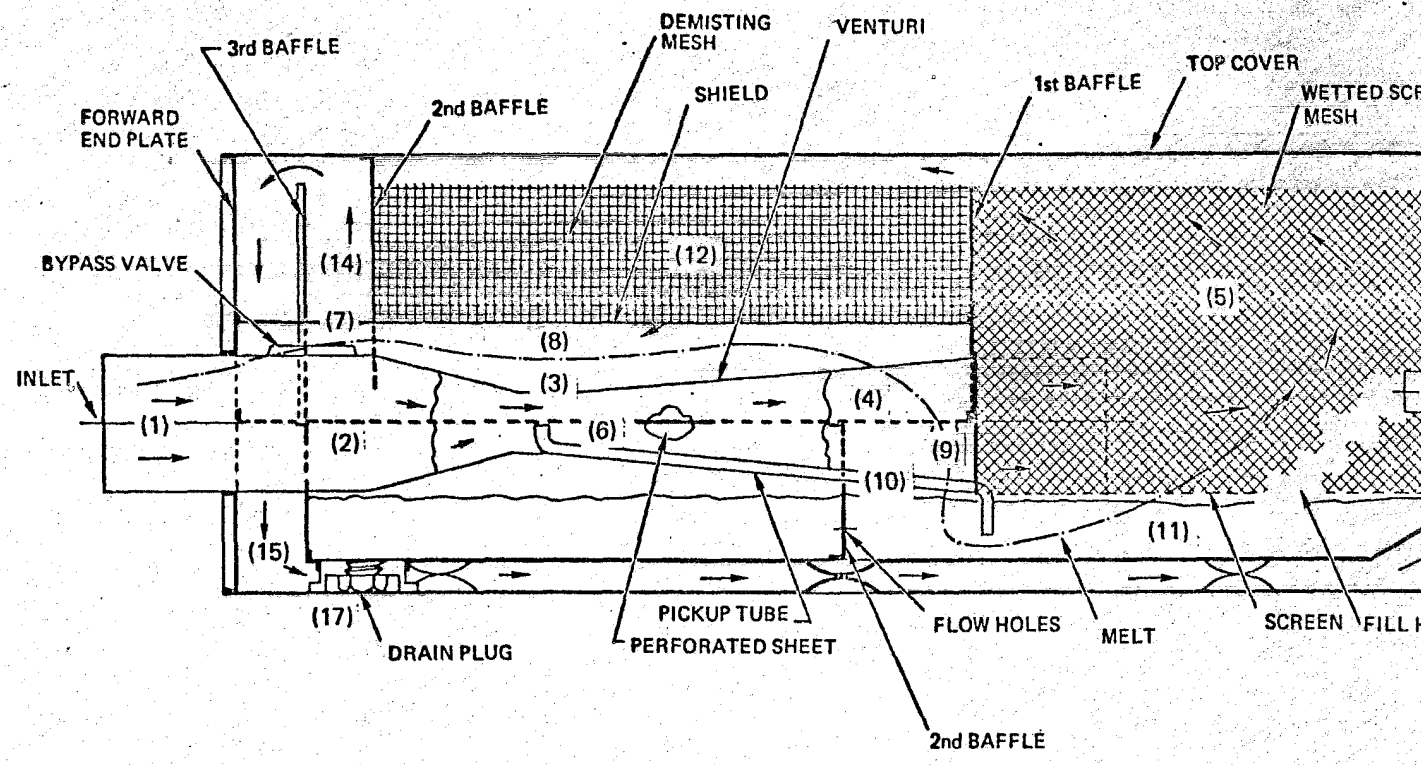


Figure 11. Muffler-Replacement Particulate Removal Device

EPI 000274

estimates which take into account lead removal by both impaction and wetted-mesh scrubbing are 99, 98, 97, and 93% lead removal at 20 mph, 40 mph, 60 mph, and wide open throttle, respectively.

Preliminary corrosion data obtained at Atomics International (under company funding) indicated that aluminized steel would probably be sufficiently corrosion resistant to contain the melt for the life of the automobile. Therefore aluminized steel was specified as the containment material. Since welding aluminized steel is difficult, the conceptual device was designed so that it could be fabricated in two halves, aluminized, and then put together with a final cold-rolled seam.

Calculations of the gas velocities at various points in the device were made at wide open throttle and are tabulated in Table VII. From these calculations, the total pressure drop across the device at wide open throttle was calculated to be about 0.6 psi (Table VIII) which is less than the pressure drop across a standard exhaust train at these gas flow rates. Therefore it appears that the pressure drop in the device will be small.

The conceptual device design was submitted to the Pricing and Estimating Division of Atomics International. They estimated that the total manufacturing cost of the device (packaged FOB from plant) was $19.58 based on two million unit/year, 2 shift operation with 250 work days/year. Computer automation of the plant was estimated to lower the device cost 15 to 20%. The cost is composed of $13.05 material, $0.27 tooling amortization and $6.26 labor. The materials cost include $2.20 salt, $6.50 mesh, $3.03 structural materials and $0.30 shipping box. No profit or installation charge is included in these costs.

EPI 000275

TABLE VII

TABULATION OF GAS VELOCITIES IN DEVICE AT WIDE OPEN THROTTLE

Location	Velocity	
	m/sec	(ft/sec)
Inlet and Outlet Tubes	131	430
Venturi Inlet and Outlet	18	58
Venturi Throat	105	345
Reaction Zone	5	16
Over 1st Baffle	69	225
Demisting Zone	4-9	13-29*
Under 3rd Baffle	69	225
Between 3rd and 4th Baffle	34	112
Over 4th Baffle	69	225
Between 4th Baffle and End Plate	34	112
Between Bottom and Outer Jacket	69	225

*Function of vertical or horizontal gas flow

TABLE VIII

TABULATION OF PRESSURE LOSSES IN DEVICE

Location	psi	Water (in.)
Venturi	0.234	6.49
Turning Losses	0.203	5.62
Exit Baffling	0.0058	0.16
Bottom Exit	0.0864	0.24
Mesh	0.072	2.0
Total	0.60	14.4

EPI 000276

VII. RECOMMENDATIONS FOR FURTHER WORK

Since laboratory tests have shown that lead can be removed from simulated exhaust in a molten salt scrubber and since an automotive test has shown that the device is compatible with various operating modes of the automobile, it is recommended that device development be continued. Our data suggest that the operating characteristics of the device on the car as well as continued laboratory tests are required. Therefore it is recommended that device testing on the automobile be continued simultaneously with laboratory testing.

Laboratory tests should be continued to more adequately characterize the lead removal efficiency as a function of flow rate, lead concentration in the gas and melt, temperature, and residence time. Continued tests of lead removal efficiency by impaction should be made to evaluate the effect of temperature and gas/liquid or gas/solid lead ratio on removal. Additional wetted-mesh tests should be made to determine the effect of packing density, surface area, temperature and melt content on the mesh on lead removal efficiency.

Automotive tests should be continued to determine the time required to melt the salt under various conditions, pressure drop through the device, melt pumping efficiency and demisting ability of the device. Several lead removal tests should be made to characterize the lead removal efficiency of the device under several different driving cycles and/or at several constant speeds. Lead removal efficiency as a function of time from cold start should be determined and estimates of lead removal efficiency for various driving cycles should be calculated from the data. Long term removal efficiencies should be determined and the recommended service frequency must be evaluated.

Corrosion tests should continue to provide adequate design data for prototype development. Several other materials should be tested and long term tests of aluminized steel should be made.

EPI 000277

VIII. CONCLUSIONS

These results show that molten carbonates are effective as a means of removing lead particles from exhaust. Both laboratory tests and tests of a device on a car confirm this conclusion. A test on an automobile showed that a molten salt scrubber is compatible with an operating automobile. Control of lead emissions by this technique would be a technical and an economically feasible (see Appendix II) alternate to prohibiting the use of leaded gasoline. This control technique has the added advantage of simultaneously reducing inorganic and organic particulates, sulfur oxide and nitrogen oxide emissions. Therefore development of this method of controlling lead emissions from spark ignition engines should be continued.

EPI 000278

IX. MOLTEN ALKALI CARBONATE EUTECTIC (APPENDIX I)

The molten alkali metal carbonate eutectic consists of 43.5 mole % lithium carbonate, 31.5 mole % sodium carbonate and 25.0 mole % potassium carbonate[1,2] which corresponds roughly to equal parts by weight of the three carbonates. This eutectic, which melts at 397°C, has been studied extensively as a fuel cell electrolyte[3-11] and as an absorbent for sulfur dioxide.[1,12-22] Consequently many of its physical,[2,3-9,26] chemical,[1,10-25,27-31] and corrosion[14,32-35] properties are known.

In addition it has been studied as an absorbent for nitrogen oxides,[23,24] lead compounds[23,25] inorganic and organic particulates[23,25] and as a reaction medium.[3,23]

A. PHYSICAL PROPERTIES

The molten carbonate eutectic is a clear nonviscous (viscosity = 10 cp) easily poured or sprayed liquid that melts at 397°C. The melt has a moderate surface tension and therefore wets most particulates. The physical properties of the molten alkalic carbonate eutectic are summarized in Table A-1.

B. CHEMICAL PROPERTIES

The chemical properties of this melt are those of a normal basic liquid. It reacts rapidly with acidic gases, liquids, and solids. Therefore, it is not surprising that it reacts with sulfur oxides, nitrogen oxides, and acidic halides such as lead chloride or lead bromide. Typical examples of reaction products are

$$M_2CO_3 + PbCl_2 \rightarrow 2MCl + PbO + CO_2 \quad \ldots(1)$$

$$M_2CO_3 + SO_2 \rightarrow M_2SO_3 + CO_2 \quad \ldots(2)$$

$$M_2CO_3 + 2NO_2 \rightarrow MNO_2 + MNO_3 + CO_2 \quad \ldots(3)$$

where M is the lithium, sodium, or potassium ion. In all three reactions the gaseous product is carbon dioxide, the normal product of carbonaceous combustion.

EPI 000279

TABLE A-1

PHYSICAL PROPERTIES OF THE MOLTEN ALKALI CARBONATE EUTEC

Property	Equation* (metric units)	Magnitude at 454°C (850°F	
		Engineering Units	Metric
Heat of Fusion (397°C)	-	11,900 Btu/lb-mole	6.6 kcal/gm-
Thermal Conductivity	-	0.242 Btu/hr-ft-°F	10^{-3} cal/cm-
Melting Point	-	747°F	397°C
Molecular Weight	-	100 lb/mole	100 gm/mole
Density	$\rho = 2.3644 - 0.5541 \times 10^{-3} T$	123 lb/ft^3	1.97 gm/cc
Viscosity	$\mu = 4.65 \times 10^{-3} \exp(11{,}000/RT)$ (425 to 625°C)	23.6 lb/ft-hr	9.76 cp
Heat Capacity	$C_p = 28.41 + 16.56 \times 10^{-3}$ (400 to 800°C)	40.44 Btu/lb-mole-°F	40.44 cal/gm
Surface Tension	$\gamma = 268.1 - 0.0694 T$§	0.01547 lb/ft	236.6 dynes/

*T in °K
†estimated
§T in °C

EPI 000280

The carbonate melts serves as a reaction medium where oxidation or reduction reactions occur. Sulfite is oxidized to sulfate, (Equation 4) organic particulates are oxidized to carbon dioxide (Equation 5) and nitrogenous compounds are reduced to nitrogen (Equation 5).

$$2M_2SO_3 + O_2 \rightarrow 2M_2SO_4 \quad \ldots(4)$$

$$MNO_3 + MNO_2 + C \rightarrow M_2CO_3 + CO_2 + N_2 \quad \ldots(5)$$

The carbonate eutectic hydrolyzes[29] to a slight extent according to Equation 6.

$$M_2CO_3 + H_2O \rightleftharpoons 2MOH + CO_2\uparrow \quad \ldots(6)$$

but the hydroxide product is even a better absorbent than carbonate for acidic materials.

The carbonate eutectic decomposes slightly at very high temperatures[11,27,28] according to Equation 7.

$$M_2CO_3 \xrightarrow[800°C]{} M_2O + CO_2\uparrow \quad \ldots(7)$$

At 800°C, the carbon dioxide equilibrium pressure is about 5 mm of mercury which is much less than the carbon dioxide partial pressure in the exhaust; therefore decomposition will not be a problem.

C. CORROSION PROPERTIES

Control of the corrosive nature of this melt has been established in both the fuel cell electrolyte program[32,33,34] and in the Atomics International development of the Molten Carbonate Process.[35] Corrosion is diffusion-limited by a passivated film that forms on the alloys. This film is self-healing and has been identified as a metal oxide, lithium chromite, or an iron-chromium spinel depending upon which metal is corrosion tested. To illustrate the noncorrosive nature of the carbonate eutectic, the corrosion rates extrapolated from 1500-hr dynamic tests were found at Atomics International[14,18,35] to be less than 10 mils/yr at 500°C for 1020 steel, Armco V iron, and 304 SS. The corrosion rate of 347 SS was < 1 mil/yr at 500°C.

EPI 000281

APPENDIX I
REFERENCES

1. L. A. Heredy, D. E. McKenzie, and S. J. Yosim, "Removal of Sulfur Oxides from Flue Gas," U.S. Patent 3,438,722 (1969)

2. G. J. Janz, Molten Salt Handbook (Academic Press, 1967)

3. G. J. Janz, "Molten Carbonate Electrolyte as Acid-Base Solvent System," AD 651604 (February 1967)

4. G. J. Janz and M. R. Lorenz, J. Chem. Eng. Data, 6, 321 (1961)

5. A. T. Ward and G. J. Janz, Electrochim. Acta, 10, 849 (1965)

6. G. J. Janz, E. Neuenschwander, and F. J. Kelly, Trans. Faraday Soc., 59, 841 (1963)

7. G. J. Janz, "Thermogravimetric and Corrosion Studies, and Phase Equilibria for Lithium, Sodium, and Potassium Carbonates," NP7015 (1958)

8. G. J. Janz and F. Saegusa, J. Electrochem. Soc., 110, 452 (1963)

9. G. J. Janz and J. L. Perano, Trans. Faraday Soc., 60, 1742 (1964)

10. G. J. Janz, J. Chem. Educ. 44, 581 (1967)

11. G. J. Janz and M. R. Lorenz, J. Electrochem. Soc., 108, 1052 (1961)

12. L. F. Grantham, L. A. Heredy, D. E. McKenzie, R. D. Oldenkamp, and S. J. Yosim, "The Molten Carbonate Process for Control of Sulfur Oxide Emissions," to be published

13. R. D. Oldenkamp and D. E. McKenzie, "The Molten Carbonate Process for Control of Sulfur Oxide Emissions," Presented at the Air Pollution Control Assoc. Meeting, Minneapolis (1968)

14. "Development of a Molten Carbonate Process for Removal of Sulfur Dioxide from Power Plant Stack Gases," PB 179 980, U.S. Dept of Commerce (April 1, 1968)

15. R. D. Oldenkamp and E. D. Margolin, Chem. Eng. Prog., 65, 73 (1969)

16. "Development of a Molten Carbonate Process for Removal of Sulfur Dioxide from Power Plant Stack Gases, Progress Report No. 2, Part I. Process Chemistry-Reduction," AI-70-5 (October 27, 1968)

EPI 000282

17. "Development of a Molten Carbonate Process for Removal of Sulfur Dioxide from Power Plant Stack Gases, Progress Report No. 2, Process Chemistry-Regeneration," AI-70-6 (October 27, 1968)

18. "Development of a Molten Carbonate Process for Removal of Sulfur Dioxide from Power Plant Stack Gases, Progress Report No. 2, Part III, Materials Studies," AI-70-7 (October 27, 1968)

19. "Development of a Molten Carbonate Process for Removal of Sulfur Dioxide from Power Plant Stack Gases, Progress Report No. 2, Part IV, Contactor Development," AI-70-8 (October 27, 1968)

20. "Development of a Molten Carbonate Process for Removal of Sulfur Dioxide from Power Plant Stack Gases, Progress Report No. 2, Part V, Fly Ash Studies," AI-70-9 (October 27, 1968)

21. "Development of a Molten Carbonate Process for Removal of Sulfur Dioxide from Power Plant Stack Gases, Progress Report No. 2, Part VI, Small Pilot Plant and Component Test Loop Design," AI-70-10 (October 27, 1968)

22. "Development of a Molten Carbonate Process for Removal of Sulfur Dioxide from Power Plant Stack Gases, Progress Report No. 2, Part VII, Plant Analysis," AI-70-11 (October 27, 1968)

23. L. F. Grantham, "Removal of Nitrogen Oxides and Other Impurities from Waste Gases," Patent pending

24. Development of the Molten Carbonate Process for Removal of Sulfur Oxide and Nitrogen Oxide in Power Plant Stack Gases, AI-70-37

25. Development of the Molten Carbonate Process to Remove Lead and Other Particulates from Spark Ignition Engine Exhausts, AI-70-47

26. M. Rolin and J. M. Recapet, Bull. Soc. France, 2504 (1964)

27. P. L. Spedding and R. Mills, J. Electrochem. Soc., 112, 595 (1965)

28. P. K. Lorenz and G. J. Janz, Private communication (1968)

29. N. Busson, S. Palous, J. Millet, and B. Buvet, Electrochim. Acta, 12, 1609 (1967)

30. R. Mills and P. L. Spedding, J. Phys. Chem., 70, 4077 (1966)

31. M. Schenke, G. H. J. Broers, and J. A. A. Ketelaar, J. Electrochem. Soc., 113, 404 (1966)

32. G. J. Janz and A. Conte, Electrochim. Acta, 9, 1279 (1964)

EPI 000283

33. M. D. Ingram and G. J. Janz, "The Thermodynamics of Corrosion in Molten Carbonates, Application of E-CO_2 Diagrams," AD 499 (1964)

34. H. J. Davis and D. R. Kinnibrugh, J. Electrochem. Soc., 117, 392 (1970)

35. L. F. Grantham. P. H. Shaw, and R. D. Oldenkamp, "Corrosion of Metals in Molten Mixtures of Alkali Metal Carbonates Containing Sulfur Compounds," In press, J. Electrochem. Soc.

EPI 000284

X. ECONOMIC CALCULATIONS (APPENDIX II)

The molten salt must be changed periodically in an automotive device in order to maintain the melting point of the mixture and to remove absorbed substance from the system. Conversion of more than 50% of the carbonate to chloride and sulfate increases the melting point of the salt excessively and allows separate phases to form. The absorbed organic particulates burn to CO_2 in the melt and the absorbed nitrogenous compounds are reduced to nitrogen by the absorbed organic particulates. These compounds do not affect the service frequency of the device. Lead and other metals form a sludge at the bottom of the salt. Therefore in order to remove chlorides, sulfates and inorganic sludge from the device the melt must be drained from the system periodically. It is assumed that 10,000 gallons of gasoline containing 3 g/gal of lead tetraethyl and 0.01 wt % sulfur is combusted throughout an automobile's lifetime (150,000 miles), then approximately eight changes of salt would be required. If it is assumed that the original device costs $50 installed and that each salt change costs $10, then the cost of controlling lead emissions by this technique is less than 1 ¢/gal or 1 mill/mile. Cost estimates for removing lead from gasoline are as high as 6 ¢/gal.

EPI 000285

XI. REFERENCES

1. R. S. Morse, "The Automobile and Air Pollution: A Program for Progress, I," U.S. Dept. of Commerce (1967), pp 10-11

2. Motor Trend Magazine, May 1970, p 48; Wall Street Journal, April 8, 1970, p 32

3. R. A. Kehoe, Arch. Environ. Health, 8, 232, 235 and 348 (1964)

4. R. A. Kehoe, J. Cholak, J. A. Spence and W. Hancock, Arch. Environ. Health, 6, 239 and 255 (1963)

5. R. H. Daines, H. Motto and D. M. Chilko, Environ. Sci. and Tech., 4, 318 (1970)

6. E. A. Schuck and J. K. Locke, Environ. Sci. and Tech., 4, 324 (1970)

7. R. G. Smith, J. Szajnar and L. Hecker, Environ. Sci. and Tech., 4, 333 (1970)

8. R. E. Lane, Arch. Environ. Health, 8, 243 (1964)

9. R. T. Johnstone, Arch. Environ. Health, 8, 250 (1964)

10. H. D. Smith, Arch. Environ. Health, 8, 256 (1964)

11. M. R. Zavon, Arch. Environ. Health, 8, 262 (1964)

12. L. W. Sanders, Sr., Arch. Environ. Health, 8, 270 (1964)

13. T. D. Sterling, Arch. Environ. Health, 8, 333 (1964)

14. L. A. Chambers, Environ. Sci. and Tech., 4, 340 (1970)

15. J. R. Goldsmith, Cal. Dept. Health — Testimony before Calif. Air Resource Board and "Epidemiological Basis for Possible Air Quality Criteria for Carbon Monoxide and Lead," presented at the Air Pollution Control Association meeting, New York 1969

16. Business Week, May 2, 1970, p 112

17. Air and Water News, March 2, 1970, p 5

18. Calif. Air Resources Board Minutes, January and March, 1970

19. Chem and Eng. News, February 16, 1970, p 29

20. Kirk-Othmer, "Encyclopedia of Chemical Technology," 10, 475 (1966)

EPI 000286

XI. REFERENCES (Continued)

21. E. N. Cole, Talk before SAE meeting, January 1970

22. Chem. and Eng. News, March 16, 1970, p 38

23. Chem. and Eng. News, February 11, 1970, p 19. Also see "Status of Lead Antiknocks in Gasoline," by F. D. Gottwald, Jr., Ethyl Corporation's Board Chairman, and "Exhaust Valve Seat Recession in Highway Operation on Unleaded Gasoline," Ethyl Corporation Publication, TS-208 (1970)

24. Chemical Week, March 11, 1970, p 14

25. Chem. and Eng. News, February 1970, p 51

26. Texaco recently announced that it would market lead-free gasoline in California at 6¢/gal above normal regular grade prices (Wall Street Journal, April 8, 1970, p 32)

27. S. D. Lawson, J. F. Moore, J. B. Rather, Jr., Hydrocarbon Process., 46, 173 (1967) or "U.S. Motor Gasoline Economics, Vol I, Manufacturer of Unleaded Gasoline," Bonner and Moore, Assoc., Inc., Houston, Texas, June 1967

28. Estimates indicate that approximately 6-10% additional petroleum crude will be required to upgrade present gasoline feed stock to regular grade without tetraethyl lead

29. Chem. and Eng. News, January 26, 1970, p 21

30. Chemical Week, March 11, 1970, p 12

31. Chemical Week, March 11, 1970, p 39

32. B. Dimitriades, B. H. Eccleston and R. W. Hurn, "An Evaluation of the Fuel Factor Through Direct Measurement of Photochemical Reactivity of Emissions," presented at the Air Pollution Control Association meeting, New York, 1969

33. L. F. Grantham, "Removal of Nitrogen Oxides and Other Impurities from Waste Gases," patent pending

34. L. A. Heredy, D. E. McKenzie and S. J. Yosim, "Removal of Sulfur Oxides from Flue Gas," U.S. 3, 438, 722 (1969)

35. D. A. Hirschler, L. F. Gilbert, Arch. Environ. Health, 8, 297 (1964)

36. D. A. Hirschler, L. F. Gilbert, F. W. Lamb and L. M. Niebylski, Ind. and Eng. Chem., 48, 1532 (1956); 49, 1131 (1957)

EPI 000287

37. R. E. Lee, Jr., R. K. Patterson, W. L. Crider, and J. Wagman, "Concentration and Particle Size Distribution of Particulate Emissions in Automobile Exxhaust." To be submitted for publication in Atm. Environ.

38. P. K. Mueller, et al., "Concentration of Fine Particles and Lead in Car Exhaust," ASTM Special Technical Publication No. 352, 60 (1962)

39. Chem. and Eng. News, March 9, 1970, p 42

40. R. I. Larsen, Arch. Environ. Health, 8, 325 (1964)

41. J. Cholak, Arch. Environ. Health, 8, 314 (1964)

42. J. M. Colucci, C. R. Begeman and K. Kumber, J. Air Poll. Control Assoc., 19, 255 (1969)

43. J. L. Barton and H. Bloom, J. Phys. Chem., 60, 1412 (1956)

44. J. Jahn-Held and K. Jellinek, Z. Elektrochem., 43, 491 (1937)

45. K. Jellinek and Golubowski, Z. Physik. Chem., A147, 461 (1930)

46. C. G. Maier, Bureau of Mines Tech. Paper No. 360 (1925)

47. D. N. Tarasenkov, A. V. Grigorovich and A. V. Bogoslovskoya, J. Gen. Chem. (USSR), 5, 924 (1935)

48. H. Von Wartenberg and O. Bosse, Z. Elektrochem., 19, 482 (1913); 27, 162 (1921)

49. "Handbook of Chemistry and Physics," U.S. Rubber Company, 48, D115 (1968)

50. C. J. Smithells, "Metals Reference Book," Vol II, 658 (1962)

51. "Report of the Swiss Leaded Gasoline Commission to the Federal Council on its Activities During the Period 1947-1960," Mitt. Geb. Lebensmittelunters. u. Hyg., 52, 135-244 (1961)

52. R. E. Lee and R. K. Patterson, Atm. Environ., 3, 249 (1969)

53. R. E. Lee, R. K. Patterson and J. Wagman, Environ. Sci. and Tech., 2, 288 (1968)

54. F. L. Ludwig and E. Robinson, Atm. Environ., 2, 13 (1968)

55. E. Robinson and F. L. Ludwig, J. Air Poll. Control Assoc., 17, 664 (1967)

EPI 000288

XI. REFERENCES (Continued)

56. J. F. Roesler, H. J. R. Stevenson and J. S. Nader, J. Air Poll. Control Assoc., 15, 576 (1965)

57. J. Wagman, R. E. Lee, and C. J. Axt, Atm. Environ., 1, 479 (1967)

58. G. J. Janz, "Molten Salt Handbook," Academic Press, New York (1967)

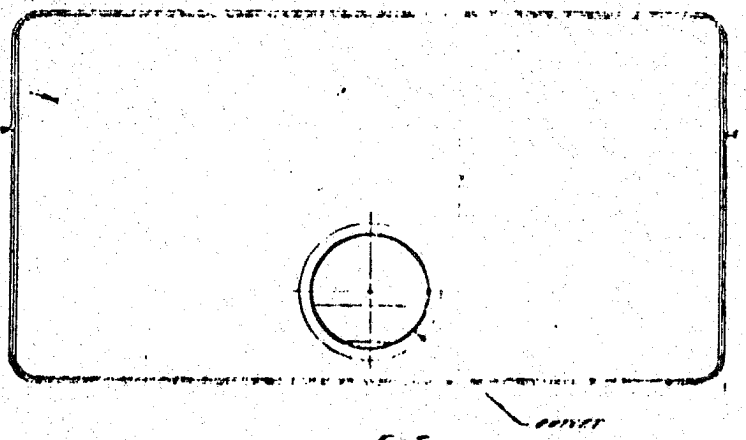
59. R. D. Oldenkamp and E. D. Margolin, Chem. Eng. Prog., 65, 73 (1969)

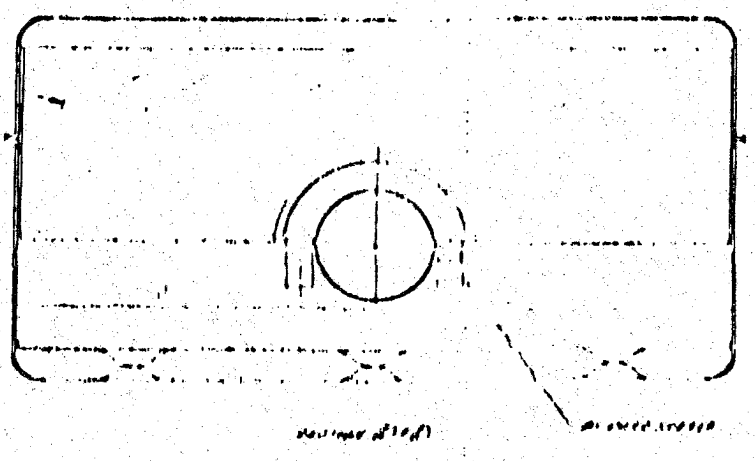
60. "Development of a Molten Carbonate Process for Removal of Sulfur Dioxide from Power Plant Stack Gases," PB 179, 909, U.S. Dept. of Commerce (1968) and subsequent progress reports AI-70-5, -6, -7, -8, -9, -10, -11 and -37.

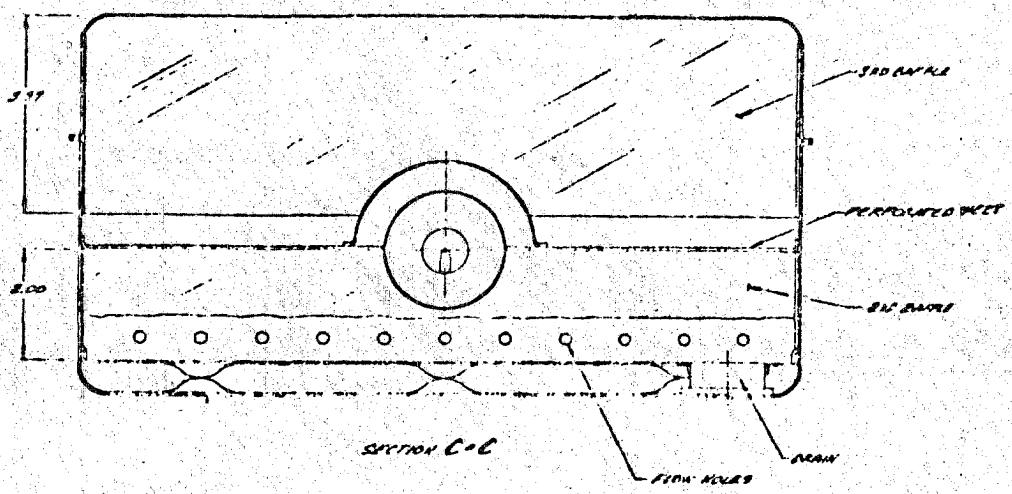
61. M. Heinen, "Vehicle Exhaust Control — Problem and Solution," Hearings before the Senate Subcommittee on Air and Water Pollution (1967), Part 1, p 443

62. Kirk-Othmer, "Encyclopedia of Chemical Technology," 2, 825 (1966)

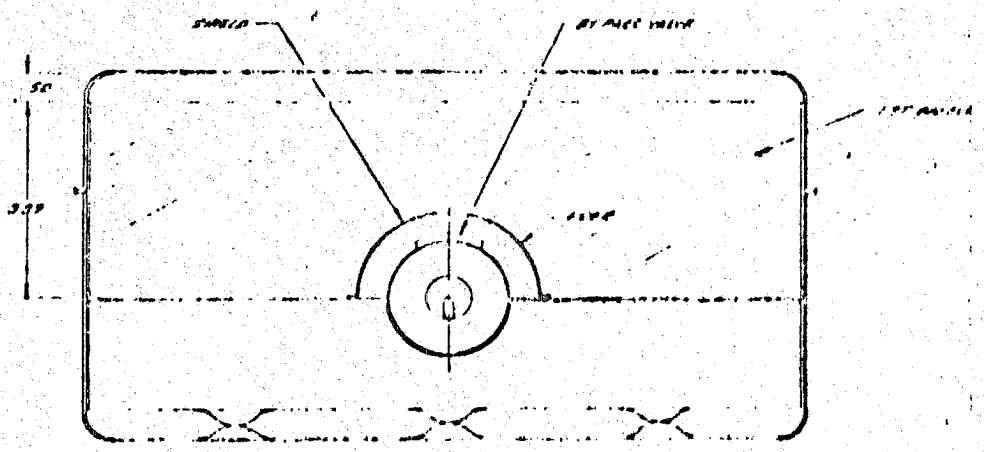
EPI 000289

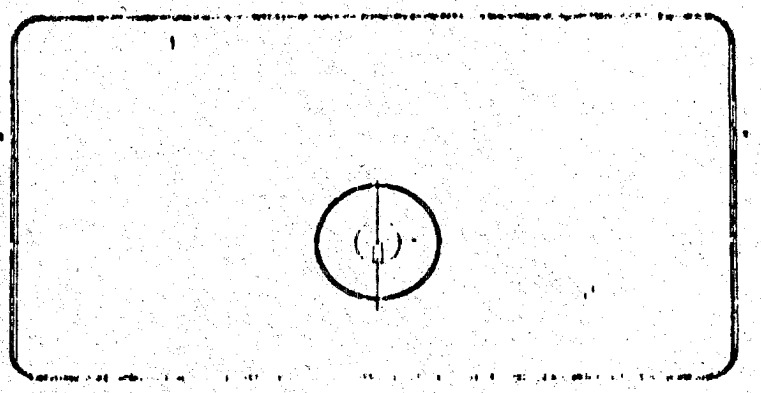


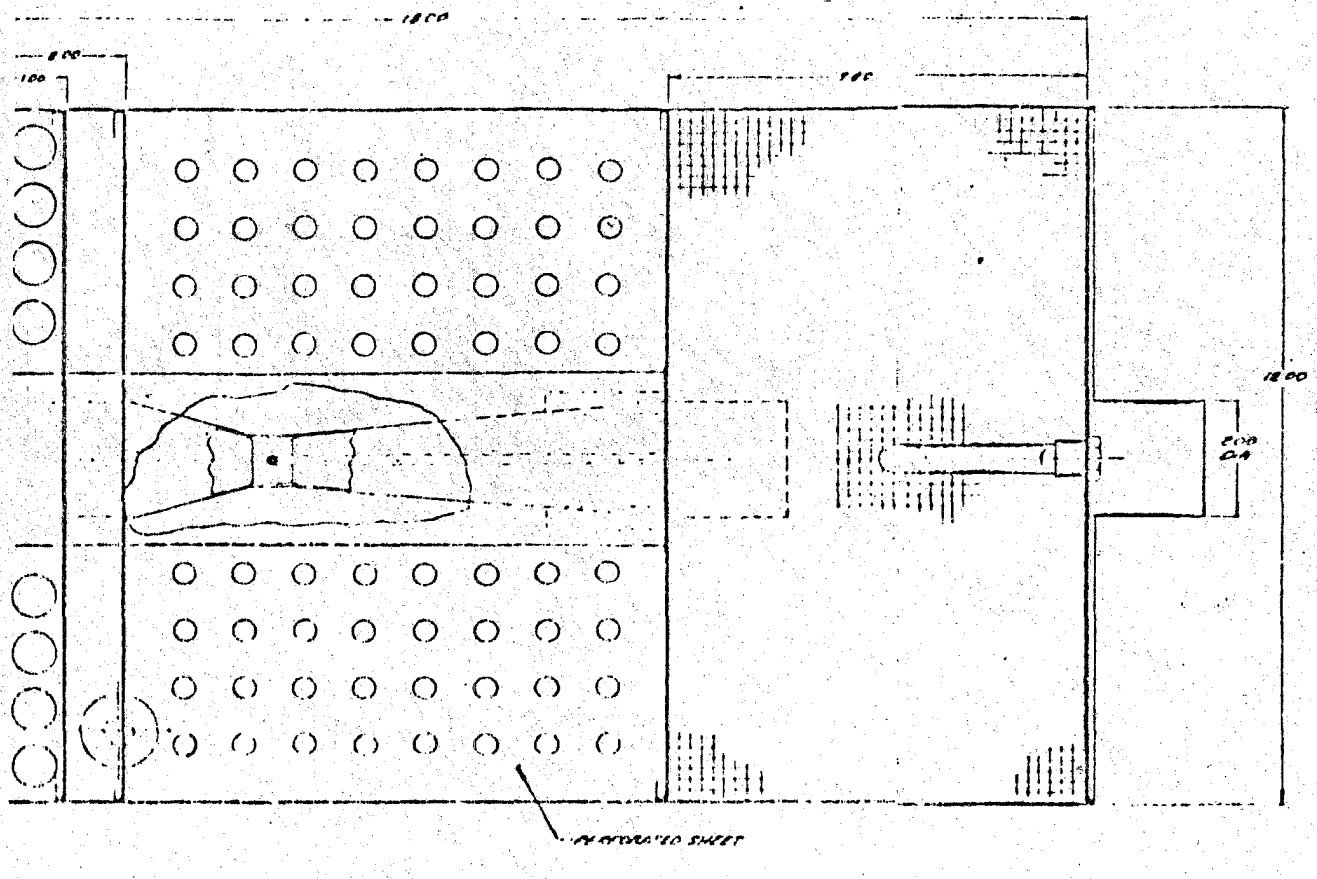


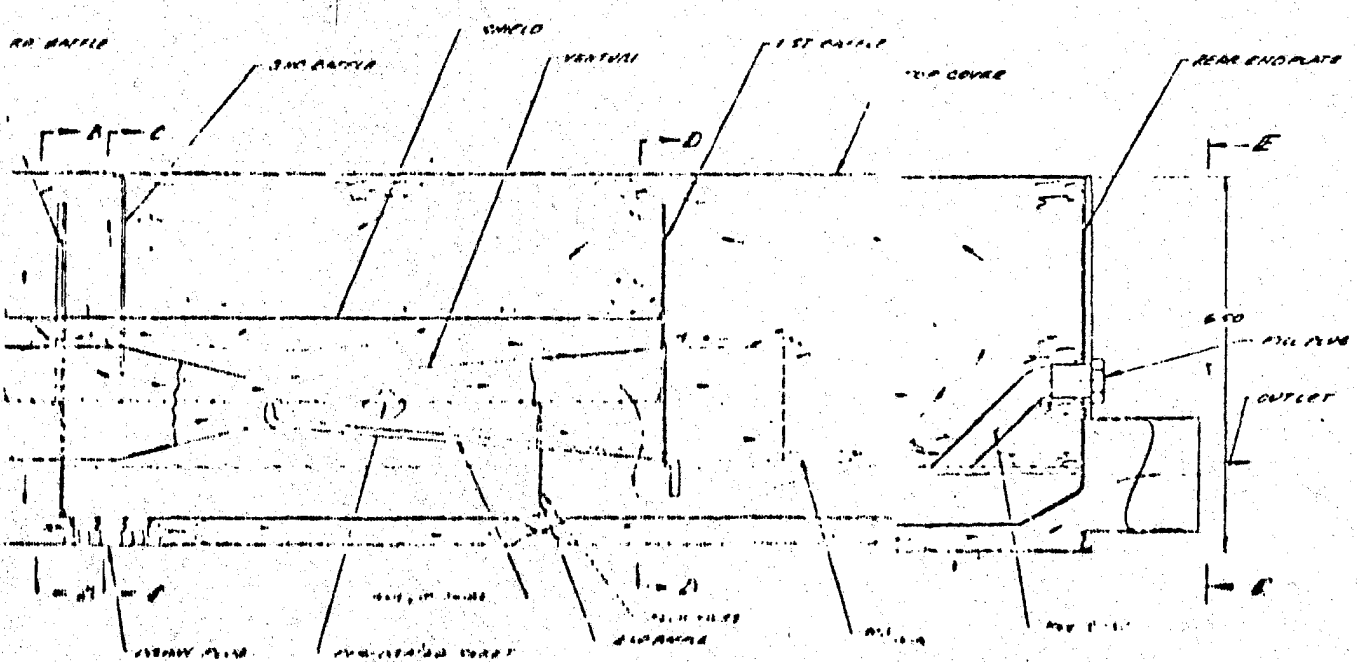

3.99
2.00
SEE BAFFLE
PERFORATED SHEET
SEE BAFFLE
DRAIN
FISH HOLES

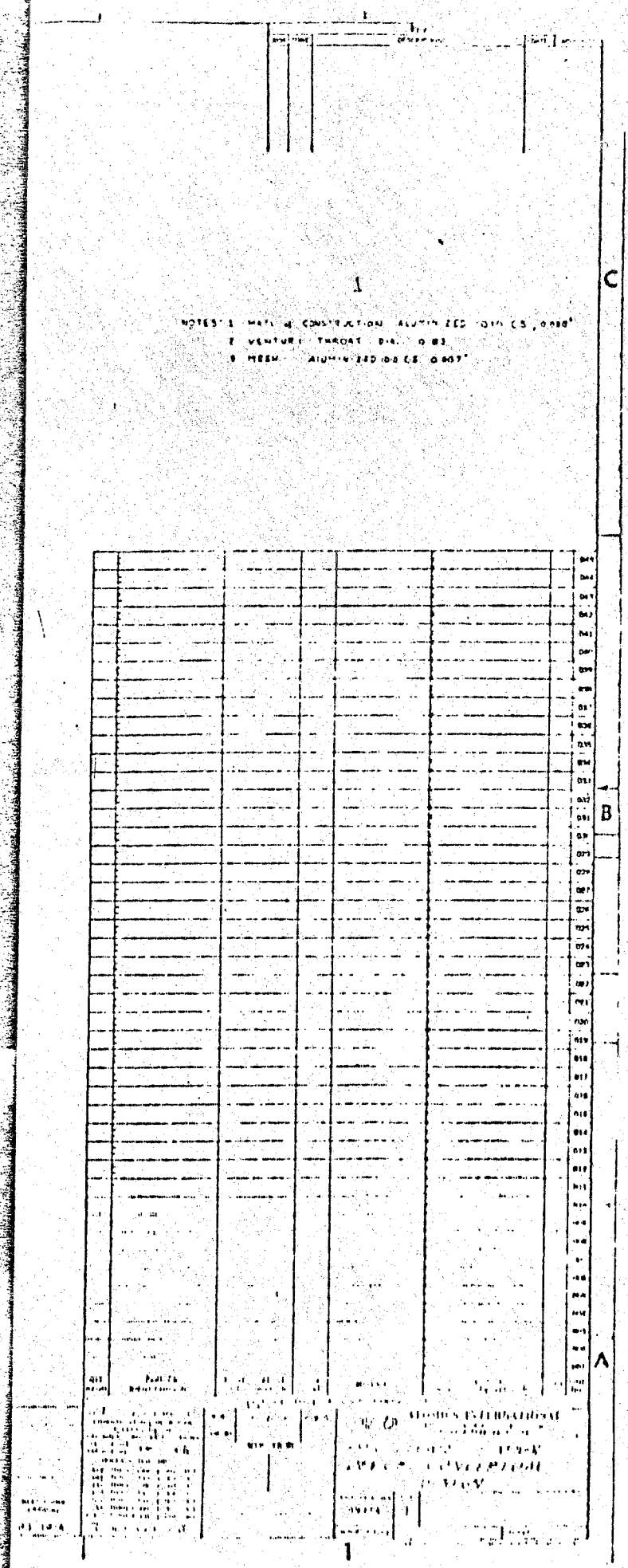
SECTION C-C


SHIELD
BY PASS VALVE
50
3.99
VANE




1800
100
700
1800
PERFORATED SHEET


RH BAFFLE
3.MM BAFFLE
VENTURI
1 ST BAFFLE
REAR END PLATE
OUTLET


C
B
A