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Separation of iron-tin alloys using gas-solid reactions

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SEPARATION OF IRON-TIN ALLOYS

USING GAS-SOLID REACTIONS

BY

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THESIS

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ACKNOWLEDGMENTS

TABLE OF ILLUSTRATIONS

LIST OF TABLES

TABLE OF CONTENTS

I INTRODUCTION

Iron-tin products from which tin could be extracted are found in many forms ranging from 0.55% [12] to 80% [2]

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(12) Oesper, Ralph E., Recovery of Tin from Tin Cans, Journal Chem. Education, Vol. 20, p. 406, 1943.
(2) Mantell, C. L., Tin.

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tin. The most important of these are: scrap tin plate, drosses from the tin plate industry, refinery drosses, and hardhead. The United States uses about 55% [26] of the

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(26) Renick, Abbott, and Umhau, John B., Tin Consumed in the Manufacture of Tinplate in 1955, Mineral Market Report, MMS. No. 2504, May, 1956.

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world's production of tin in making tin plate of which there are two types, electrolytic which contains 0.55% [12] tin and hot dipped which contains between 1% and 1.5% [12] tin. The scrap, a total of 578,324 [27] long tons in 1955,

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(12) Oesper, Ralph E., Recovery of Tin from Tin Cans, Journal Chem. Education, Vol. 20, p. 406, 1943.
(27) Renick, Abbott, and Umhau, John B., Tin Recovered by Detinning Plants in 1955, Mineral Market Report, MMS. No. 2505, May, 1956.

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consisted of 98.9% clean tinplate clippings and the balance of old tin coated containers. Drosses from the tin plate industry occur when crystals of the composition

$FeSn_2$ [8] form and break loose from the base metal. These

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(8) Romig, O. E., Constitution of the Fe-Sn Alloys, Metal Progress, Vol. No. 42, pp. 899-904, 1 42.

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crystals once broken loose from the base metal float on the surface as a dross which is removed periodically. Refinery drosses containing about 65% [2] tin are produced at the surface of the reduced alloy of high tin content when it is cooled to just above the melting point of tin. In usual practice this dross which amounts to about 5% [2] of the metal reduced is skimmed from the tin and is fed back to the first reducing furnace. Hardhead is the name given to alloys of iron and tin originating from the smelting of tin. They have no definite composition but consist of tin intermingled with $FeSn_2$ and usually contain some arsenic. They are usually thought of as containing 80% [2] tin although analysis as low as 17.9% [2] tin have been given.

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(2) Mantell, C. L., Tin, Reinhold Publishing Corp., pp. 253-254, 1949.

For years it has been a problem to the tin smelting, plating, and detinning industries to be able to separate iron from tin once they were associated together as described above. Due to the lack of a tin smelter in the United States in the past, and the abundance of tin scrap available, which had little value either for the iron content or the tin content in their untreated state, most

interest was concentrated on seeking methods of separating this tin scrap into its two useful components, iron and tin, rather than deal with the problems of smelting tin from tin ore. Since the United States now has the world's largest tin smelter located in Texas, and the quantity of tin scrap has been increasing, an the problems of both the detinner and the smelter are similiar, the interest in finding better ways of separating iron from tin has likewise increased.

The project was selected by the Mississippi Valley Experiment Station of the United States Bureau of Mines in conjunction with their extractive studies on tin. A fellowship agreement was set up between the United States Bureau of Mines and the Missouri School of Mines to enable this work to be accomplished. It was the purpose of this thesis to investigate various gas-solid reactions which may lead to new treatment techniques in industry. The field of gas-solid reactions was selected because of the scant research that has been performed in this field and the great promise this type of reaction has to offer.

II LITERATURE SURVEY

Many ideas have been presented on ways to separate iron from tin depending on the type of material to be treated. These ideas generally may be classified according to the following processes: mechanical, intermetallic separations, selective dissolution, smelting and fuming, and gas treatments. So as to give a general picture of the field of iron-tin separations, a few examples of each of the above types of processes will be given; however, a complete summary will be given for the processes of gaseous treatment.

A. INTERMETALLIC SEPARATIONS

In the class of intermetallic separations there are two technics, one removes the iron from the tin using aluminum as the addition element and the other removes the tin from the iron using lead or a similiar element. Gat [28] claims that upon adding aluminum to the molten iron-tin alloy, rich in iron, an iron-aluminum intermetallic compound of the composition Fe_2Al_3 forms which precipitates out when cooled to a temperature just above that of molten tin. The Fe_2Al_3 being less dense than tin after precipitating from solution rises to the surface of the melt as

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(28) Gat, John D., Process for the Separation and Recovery of Metals from Metallic Alloys, Pat. No. 2,290,549, July, 1942.

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a dross. The Goldschmidt Co. [29] devised the method of

removing tin, when alloyed with ferrosilicon to the extent

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(29) Goldschmidt, A. G., Process for the Utilization of Fer-
ro-Silicon Masses Containing Valuable Metals, Pat. No.
251,268, Jan., 1927.

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of 2% by adding lead to the molten alloy. The lead being

insoluble in ferrosilicon and having a greater density than

the ferrosilicon forms an immiscible layer at the bottom

of the container. The tin being more soluble in lead than

in ferrosilicon preferentially dissolves in the lead by dif-

fusing through the liquid ferrosilicon and into the lead

layer. Jordon, [30] also using lead to dissolve the tin,

operated at a temperature below the melting point of the

iron-tin alloy. First he granulated the alloy in water,

then removed any oxide films with hydrogen or any silicate films with $ZnCl_2$ flux and finally added lead to dissolve the tin. For an alloy containing 12.25% tin, an

amount of lead equal in weight to the alloy was added at a

temperature of 1800 F. The lead tin alloy produced con-

tained 10.02% tin and there was 2.07% tin left on the iron.

By again treating the iron residue with a clean portion of

lead, the tin content could be further reduced.

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(30) Jordan, J. F., Process for the Extraction of Tin from
Iron Alloys, Pat. No. 2,474,979, July, 1949.

B. SMELTING AND FUMING

A method of smelting the iron tin alloy under controlled
conditions so as to cause the iron to be oxidized and go
to form a slag, leaving the tin behind as molten metal,
was also devised by Jordan.[31] The iron-tin alloy is

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(31) Jordan, J. F., Method of Refining Tin Metal, Pat. No.
2,441,768, May, 1948.

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melted with a thin layer of slag, to protect it, at a
temperature above 2400°F. With a basic slag, the iron oxide
content should not be allowed to exceed 50%. Only when the
iron content of the metal is around 25% should this be
exceeded. Also the iron content of the slag is decreased
as the iron content of the metal decreases. The operation
is stopped when the tin formed contains only a small per-
centage of iron (5%) so that drossing is economical. The
oxidizing characteristic of the slag is controlled by the
addition of Fe_2O_3 which is the chief source of oxygen.
Osborn [32] devised a method of separating iron from tin
which involves first smelting the material with enough
carbonaceous material to produce pure tin and a slag rich in
iron and tin. This slag is subjected to blowing with air
which contains fuel oil, and finely divided pyrite. All the
tin present is reduced and subsequently sulfidized and vola-
tilized from the slag. At the surface of the slag, the

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(32) Osborn, W. H. (to Phelps Dodge Corp.), Tin Recovery
Process, Pat. No. 2,304,197, Dec., 1942.

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volatilized tin sulfide is oxidized to tin oxide and then collected as fume by conventional means. Another method of smelting developed by Porter [33] converts the iron into

(33) Porter, Carroll B. (to American Smelting and Refining Co.), Pat. No. 2,364,815, Dec., 1944.

the sulfide which dissolves in a soda slag thus leaving the tin relatively free from iron. An alloy containing 85% tin and 7% iron, smelted at 1800 F. with coke and sodium carbonate produced a resultant metal containing 94.8% tin and 0.35% iron. The slag had 21.3% tin and 29.9% iron. The tin in the slag represented 5% of the total tin charged to the smelter. This slag is then resmelted with coke to produce a slag low enough in tin to be discarded. The Goldschmidt Company [23] smelted the tin bearing material with an alkali to produce a stannate. This stannate was then reduced to finely divided tin metal by passing CO_2 through it. The finely divided tin was converted first to oxide and then worked up into tin blocks with a reducing flame. Richter [34] performed a similar smelting operation with alkali but did so to produce the water soluble stannate.

(23) Goldschmidt, A. G., Tin, Pat. No. 620,711, Oct., 1935.
(34) Richter, Hartmut W., Separating Tin and Lead from Materials such as Alloys, Pat. No. 2,145,433, Jan., 1931.

C. MECHANICAL

Alloys high in tin can have some tin removed by filtration. It is not practical, however, to filter tin which contains much more than 6% iron, for the fluidity of the metal decreases above this percent and much tin is then held by entrapment in the $FeSn_2$ crystals. Lepsoe and Jones [35] worked on equipment that could be used to perform this filtration. They found that asbestos cloth made the best filtering medium. Starting with tin that contained 0.4% iron, filtering at a temperature of 350'C., produced a tin bullion with an iron content of less than 0.007%. The rate of filtering is about 4.5 pounds of tin per minute per square inch of filtering surface. Investigations carried on by the United States Bureau of Mines [37] used a brass

(35) Lepsoe, Robert and Jones, Edward L., (to Consolidated Mining and Smelting Co. of Canada.), Pat. No. 2,450,865, Oct., 1948.
(37) St. Clair, H. W., Refining Metals and Alloys by Filtration, U. S. Bureau of Mines Report, Invest No. 4614, 1949.

screen with 3600 meshes per square cm. heated in a porcelain tube. The metal was forced through with air pressure. Other filters were used such as porous chamotte stones or porous aerolith stones. It was ound, however, that if these porous stones were used whole the pores would seal up after a short time of operation; therefore, the stones were granulated. The granulated filter stones were placed 3-5 cm. deep on a perforated iron or chamotte plate starting with 3mm. stones at the bottom and finishing with 0.3mm.

stones at the top. To prevent the bed from rising, another
iron or chamotte plate was placed on top. If iron plates
were used, they would be coated with aluminum oxide to pre-
vent them from being attacked. The filter cake obtained
was 80% tin, 9.5% iron, or 52.5% $FeSn_2$. This corresponded
to a yield of 97% of the tin from bullion containing 0.4%
iron. Bullion up to 6% iron has been filtered successfully.
Instead of filtering, Graves [36] treated the iron contamina-
ted tin producing a dross high in iron with the residual

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(36) Graves, Ritson H., (to American Metal Co., Ltd.),
Pat. No. 2,363,127, Removal of Iron from Tin, Nov., 1944.

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tin content less than 0.01% iron. He charged tin contain-
ing 2.8% iron, into a 30-ton open kettle in which a small
amount of pure tin was left from the previous treatment
cycle. The temperature was raised to 1100° F. while stirr-
ing it with a mechanical stirrer in the presence of air for
one and a half hours. At the end of this time, a dross was
removed analysing 54.5% tin and 25.1% iron. Another addi-
tion of tin containing 3.82% iron was added which was
treated the same as the first addition giving a dross with
43.4% tin and 26.9% iron leaving the refined tin analysing
at 93.23% tin and 0.01% iron. The refined tin is removed
for casting leaving a small amount remaining to start the
next cycle.

Kroll, Lissauer and Cie [38] separated iron from alloys by employing the use of a powerful magnetic field. The alloy was allowed to solidify slowly between poles of powerful electromagnets, the iron concentrating where the field is the strongest. This concentrated portion high in iron was removed by mechanical means such as shears or presses. By repeating the process again and again the percent residual iron can be lowered to a tolerable limit.

D. SELECTIVE DISSOLUTION

By using a water solution of caustic and an oxidizing agent a selective dissolution can be attained, for the caustic will only attack the tin forming sodium stannate leaving the iron unattacked. The solution thus obtained is thickened to remove lead and then fed to electrolytic cells to recover the tin [39]. Hickey [22] claims that adding 3%

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(38) Kroll, Wilhelm and Lissauer, M and Cie, Removing Iron from Alloys, Ger. Pat. No. 483, 431, Dec., 1928.
(39) Renick, Abbott and Umhau, John B., Tin, Bureau of Mines Bulletin 556, 1955.
(22) Hickey, Elmo G., Process of Recovering Tin, Pat. No. 1,592,935, July, 1926.

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ammonium hydroxide (28%) to the caustic bath, containing 4 to 12% sodium nitrate and 18-28% sodium hydroxide, decreases the detinning time from 6-7 hours to one hour.

Worsey [25] describes a method where an aqueous solution of

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(25) Worsey, Jos. F., Recovery of Tin from Tin Plate Clippings, Min. and Scient. Press, Vol. 83, 1901.

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hydrogen chloride is used to dissolve the tin from tin plate. Sulfuric acid is introduced to increase the efficiency of the hydrogen chloride. The tin is recovered by adding old galvanized iron to reduce the tin which floats to the surface upon diluting the solution.

E. GAS TREATMENTS

1. Chlorine

Gases have been mainly used in the detinning of tin plate and only in a few instances have they been used in treating "hardhead" or similar material. Chlorine is of the greatest significance and dates back to 1854. The first commercial detinning plant, which lasted but a short time, was established in New York in 1873. In 1907 detinning came back into importance with Goldschmidt and his chlorination process of detinning.

Many patents were issued at this time describing various phases of the chlorination process and versions of apparatus to be used in removing the tin from iron when associated, usually as tin-plate. The underlying principle in most of the patents is to convert the tin to stannic

chloride by the reaction;

$$Sn + 2Cl_2 \rightarrow SnCl_4$$
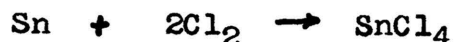
and not attack the iron. This is accomplished by not allowing the temperature to rise to a point where the chlorine can attack the iron ($38^{\circ}C$) and also to use chlorine which is moisture free. If any iron is attacked it is done so by the following reaction;

$$Fe + 3/2Cl_2 \rightarrow FeCl_3$$
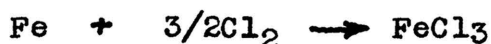
Any chlorides remaining on the scrap must be removed either by volatilization or by washing the scrap with water. This is necessary in order to obtain high recovery of tin and also prevent the iron scrap from rusting so it will be salable.

One of the difficulties encountered with the use of chlorine is to control the temperature throughout the reaction vessel so that it won't exceed 38° C. A few methods have been patented to try and prevent this. Zacharias [40] ob-

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(40) Zacharias, Walther, Chlorin Detinning Process, Pat. No. 1,283,016, Oct. 1918.

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served in using a specially designed glass reactor that the reaction between the tin and the chlorine didn't take place until a rather high concentration of chlorine was present which could be observed by the color in the reactor. When this high concentration was reached the reaction started thus producing heat. The heat causes the temperature

to rise suddenly thus causing iron to be attacked as well as tin. The reaction appeared to start at a single point in the chamber and spread quickly thru-out. To get away from this, he suggested having finely divided tin placed on top of the scrap to trigger the reaction at a lower chlorine concentration so that the temperature of the reaction wouldn't get out of and. Goldschmidt and Weber [41] believed that the attack on iron was due to "hot-spots" developed in the column of scrap. To prevent this, they patented a method by which the chlorine would be circulated in a whirling motion through a specially designed multi-compartment reactor. They also made provision for the chlorine to go through a heat exchanger to remove some of the heat from the gases if their temperature rose above tolerable limits. They believed that this vigorous agitation would prevent the "hot-spots" from forming thus preventing the chlorine from attacking the iron. Linde [42] describes

(41) Goldschmidt, Karl and Weber, Josef, Detinning Tin-Scrap, Pat. No. 1,158,128, Oct. 1915.
(42) Von Der Linde, Carl, Process of Detinning Tin Scraps, Pat. No. 981,775, Jan., 1911.

in a patent that in order to prevent attack of the iron the chlorine should not be added continuously, but in time intervals of 15 minutes each. Wolff [43] prevents overheating

(43) Wolff, P., Improvements in Obtaining Tetrachloride of Tin from Tin Scrap and other Materials Containing Tin, Pat. No. 18,329, 1909.

by passing the chlorine into the reactor slowly. He claims that this has the same effect as diluting the chlorine with an inert gas. Carrier [44] devised a multiple

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(44) Carrier, C. F., (to Vulcan Detinning Co.), Method of Detinning, Pat. No. 1,358,136, Nov., 1920.

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step process in which the fresh tin scrap is first brought in contact with dilute chlorine, thus removing a good portion of the tin. Due to this low concentration of chlorine while the concentration of tin is the highest, the temperature remains stable and does not suddenly rise to where the iron is attacked. In a few steps the concentration of the chlorine is increased to 100% and the last traces of tin on the scrap are removed. Kugelgen and Seward [45] control the temperature by limiting the quantity of scrap to an amount that will not cause a given size reaction vessel to become overheated.

Schutz [47] modified the chlorination process in that

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(45) Von Kugelgen, F. and Seward, G. O., Process of Detinning, Pat. No. 851,946, April, 1907.
(47) Von Schutz, H ans, Process of Detinning Tin-Plate by Means of Chlorin, Pat. No. 940,898, Nov., 1909.

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he created a vacuum around the tin scrap and admitted the chlorine in small additions so that the vacuum would not be completely destroyed. This procedure also prevented sudden temperature rises which would cause attack on the iron.

Another unique method of controlling the rate of the reaction was invented by Leitch [48]. He placed the scrap

(48) Leitch, M., (to Metal Process Co.), Method of Detinning Tin-Scrap, Pat. No. 883,411, March, 1908.

in a reaction vessel into which he pumped tin tetrachloride from the bottom to exclude all air. Chlorine was then connected to the top and the tin tetrachloride pumped slowly back into the reservoir. The rate at which the tin tetrachloride was pumped governed the quantity of scrap exposed to the chlorine and likewise the speed of the reaction. With this equipment, a close control could be maintained on detinning conditions. Acker [49] had a similar idea. Weber [46] takes a different slant on chlorination of the tin plate and claims that it is more economical to operate at a higher temperature than 38°C so that approximately 20% of the chlorine will react with the iron. He claims that the loss of chlorine and the impurity of the product is offset by the cost of labor to control the temperature at 38° C in the conventional processes.

Zwingenberger [50] patented a method to tie up the

(49) Acker, Charles E., Process of Detinning, Pat. No. 862.860, Aug., 1907.
(46) Weber, Josef, Process of Detinning, Pat. No. 1,115,262, Octb., 1914.
(50) Zwingenberger, Otto K., Art of Detinning Tin-Scrap and the Like Material, Pat. No. 1,260,119, March, 1918.

water vapor in the chlorine so it would not cause any damage

in detinning. He found that if sulfur dioxide was added to the chlorine, any water vapor present would react with the sulfur dioxide as follows;

$$SO_2 \; + \; 2H_2O \; + \; Cl_2 \; \longrightarrow \; H_2SO_4 \; + \; 2HCl$$
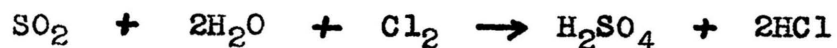
A determination of the water content is first made and then sulfur dioxide is added in a slight excess of that necessary to take care of the water; usually about 5%.

Reed [51] first removed the tin from the tin-plate by tumbling the scrap with sand, salt or some other inert material, then screening the powdered material from the scrap and finally chlorinating the tin away from the inert material.

D. A. Wilcox and S. H. Wilcox [52] patented a method of converting all the scrap into its chlorides. The chlorides can then be separated by distillation or electrolysed in aqueous solution. The tin will come out first in an electrolytic cell. Other means were also proposed for their separation.

2. Chlorine and Air

A mixture of chlorine and air was used to control the reaction and prevent the "hot spots" from occuring. Goldschmidt and Weber [53] compressed the scrap into bundles

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(51) Reed, Charles J., Process of Detinning, Pat. No. 958,177, May, 1910.
(52) Wilcox, Daniel A., and Wilcox, Sidney H., Utilization of Tin-Scrap, Pat. No. 1,310,381, July, 1919.
(53) Goldschmidt, Karl and Weber, Josef, Process of Detinning, Pat. No. 12,956, May, 1909.

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and placed these into their reaction chamber. Chlorine was
introduced and allowed to mix with the air in the chamber.
In this way, the chlorine would be dilute and would not
cause a vigorous reaction with the scrap. At the end of the
reaction, in order to get the tin remaining in the tight
crevices, the pressure was increased thus forcing the
chlorine into those crevices to attack the tin. Instead of
letting the chlorine mix with the air 'n the reaction cham-
ber, Linde [54] allowed the chlorine to pass over hollow
Guttmann's balls which contained air to ensure a homogeneous
gas mixture. This he claimed prevented "hot spots" from
forming due to local concentrations of chlorine.

Mitchell [55] patented a method for treating residues

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(54) Von Der Linde, G., Process of Obtaining the Tin from
Waste Tinned Metal, Pat. No. 1,116,176, Nov., 1914.
(55) Mitchell, Thomas A., Method of Recovering Tin from
Residues, Pat. No. 1,961,065, May, 1934.

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and oxides of tin contaminated with iron. He first reduced
these oxides to form an iron tin alloy in a granulated form
by making up a charge of the oxides, a reducing agent and
silica, and heating this charge to $600 - 900^\circ$ C in a ro-
tating kiln. The tin and iron are reduced to alloy in
small particles held apart by the inert material (silica)
in the charge. This charge is then pulverized and placed
in a chlorinating chamber, heated to between 115 and 300° C.
Chlorine and oxygen are admitted in a ratio so as to convert
the tin to stannic chloride and decompose any ferric chlor-
ide formed to the oxide. The stannic chloride formed is a

gas at the temperature of operation and is removed by distillation, being condensed in the usual fashion. He claims the invention may be also utilized for treating hardhead by first granulating it in water.

3. Oxygen

Oxygen has been blown through the molten iron tin alloy in a bessemer converter or the like to attempt a separation. Jensen [7] started with an alloy containing 20% tin, 60% iron, the balance copper, nickel, arsenic, antimony, and lead melted in a converter heated with coke. The alloy melted and trickled down through the coke. When all melted, it was blown at white heat. Three products were obtained:

1) Flue dust -- 60% tin

2) Converter slag -- 5% tin, 60-70% FeO

3) Hard tin -- 90% tin, 10% iron

One third of the tin was distributed to each of the products. M. Levy and D. Ewen [3] performed similar experiments with results in the order of those found by Jensen. Davis [16]

(7) Jensen, C. W., Treatment of Tin Smelter By-Products, Mining Magazine, Vol. 82, pp. 73-75, 1950.
(3) Levy, D. M., and Ewen, D., The Bessemerizing of hardhead, Trans. Inst. Min. and Met., Vol. 18, p. 466, 1909.
(16) Davis, P. W., Method of Refining Tin, Pat. No. 1,514,443, Nov., 1924.

patented a method of treating molten tin containing iron alloyed with it. He melted the alloy in a furnace and then bubbled oxygen or oxygen and air through the molten metal. In a short while, he claimed, practically all the iron was

oxidized leaving the tin relatively free of iron.

Phelps [56] heated tin scrap to a cherry red and then

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(56) Phelps, W. J., Detinning Tin-Scrap, Pat. No. 1,202,866, Oct., 1916.

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passed air over it and volatilized the tin as the oxide.

The conditions were regulated to prevent appreciable oxi-

dation of the iron. The vapors were cooled and collected

by the usual means. Hill [57] used the same method but

did not heat the scrap to a temperature high enough to

cause the oxide to volatilize. It was then removed by

fused sodium carbonate or caustic by converting all to a

liquid.

4. Hydrogen Chloride

Hydrogen chloride was used by Martin [14] who first

plunged the scrap into potassium hydroxide and then treated

it with the gas to produce stannous chloride at a tempera-

ture of 65° C. DeLape [15] deposited a film of water

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(57) Hill, B. W., Recovery of Tin, Pat. No. 2,268,484, Dec., 1941.
(14) Martin, M., Recovering Tin from Tinplate, French Pat. No. 958,018, March, 1950.
(15) DeLape, D. E., Process for Recovering Tin from Tin Plate, Pat. No. 2,096,090, Oct., 1937.

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on the tin plate first and then reacted it with hydrogen

chloride. He controlled the temperature so it would not

go above 50° C especially at the end of detinning for then

iron would be attacked.

5. Hydrogen and Steam

Wiltereck [18] patented a method of removing tin from

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(18) Wiltereck, H. C., Detinning Ger. Pat. No. 261,522, Feb., 1912.

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tin scrap with hydrogen and steam at a temperature of 400° C. The tin remains as the metal and drains to the bottom of the chamber while the surface of the iron is converted to Fe_3O_4 with the liberation of hydrogen. The hydrogen protects the tin from being oxidized.

6. Inert Gases

Welch and Sheek [19] patented a method to volatilize

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(19) Welch, H. V., and Sheek, A. W., Recovering Values from Tinned-Iron Wastes, Pat. No. 1,446,953, Feb., 1923.

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the tin from the scrap using large volumes of inert gas. Their furnace consisted of a vertical shaft longer than a cupola so as to allow sufficient time for the hot gases to volatilize the tin. A charge made up of a reducing agent, such as coke, scrap, and possibly some flux, is fed into the top of the furnace. As the scrap drops, the temperature increases to a point where the tin is volatilized just before the scrap melts. The iron, relatively free from tin, is tapped from the bottom. Air is injected through tuyeres also at the bottom to supply the necessary gas. It is possible at the melting point of the scrap for

the gases to contain 1/800 of a volume of tin vapor which means
that for one pound of scrap containing 2% tin, it will require
at least five pounds of hot gases. A chloridizing agent may
be added either as a gas or solid to assist in the removal
of the tin. The tin or tin compound is collected by con-
ventional means.

7. Organic Gases

Dekker [21] claims he can remove tin from tin plate
scrap by treating it with a vaporized lower aliphalic acid
in the presence of oxygen or air. The reaction progresses
at 80° C or above producing an organic salt from which
an aqueous suspension of tin oxide or hydroxide is obtained
when the scrap is rinsed with water.

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(21) Dekker, Pieter, Recovery of Tin from Tin Coated Metals,
Ger. Pat. No. 604,463, Oct. 1974.

III EXPERIMENTAL

A. PREPARATION OF ALLOYS

For the preliminary study of the reactions of gases on the solid iron tin alloy rectangular prisms (1/4 x 1/4 x 1/2") were made. First a mixture of 75% tin 99.99% grade and 25% electrolytic iron was alloyed at 1200° C in a graphite crucible and chill cast in the form of a slab approximately (10.2 x 1.7 x 17.7 cm.) in an iron mold. The prisms were sawed from the slab and machined to size on a vertical milling machine. Finally the surfaces were finished by hand grinding on "0" metallographic paper. Before use, they were washed in acetone and dried in a desiccator so as to be free of moisture and grease.

Iron-tin alloy shot was prepared by blowing the molten alloy with steam into a steam atmosphere with a specially designed piece of apparatus Fig. 1. It consists of a six KVA induction furnace inverted from the usual operating position and fitted with a carbon funnel machined from a 2 1/2 inch diameter graphite rod. The hole in the bottom of the funnel was 1/8 inch in diameter and centered so that the metal stream fell directly in the center of the ring having the steam jets, as pictured in Fig. 2. The steam jet holes, 3/64 inches diameter in the ring were bored at such an angle that the metal was blown down into the receiving drum instead of being blown back toward the furnace. At first, the holes were bored at 45° to the plane of the ring, but this caused part of the metal to be blown back of the ring,

Figure 1 Blowing Apparatus for Making Metal Shot

Figure 2 Ring with Steam Jets

therefore it was modified to what is shown in Fig. 2. The drum filled to the first ring with water was used to catch the alloy shot and also hold a protective non-oxidizing atmosphere of steam. In operation, the ring with the steam jets was inside the drum; however, in Fig. 1 the drum is lowered so that the position of this ring can be seen.

The metals were first alloyed together in a clay bonded graphite crucible at a temperature of 1200° C. The alloy was made up of 25% electrolytic iron and 75% tin, 99.99% pure. The steam was turned on to give a pressure of 50 pounds per square inch on the gauge. When the funnel reached 1200° C, the molten alloy was poured through. From 2824 grams of alloy, a total of 2790 grams of shot was produced of which 1104 grams was less than 48 mesh. The analysis of the -48 mesh shot was 72.91% tin, 26.45% iron.

B. PRELIMINARY QUALITATIVE INVESTIGATIONS OF GAS-SOLID REACTIONS

1. Equipment

The preliminary investigations were carried out using tube furnaces (Fig. 3) fitted with 5/8 inch vycor tubes. The ends of the tubes were sealed with rubber stoppers which in one end were bored to fit a glass "Y"; those at the other end had a straight piece of glass tubing. Helium was introduced through one side of the "Y" and the reactant gas through the other. The product gases left through the straight tube at the other end and entered a 50ml. florence flask and then into a water trap, which was another 50ml.

florence flask, so as to seal the system from the air. The iron-tin alloy prisms (as described previously) were placed in the center of the furnace with the Pt.-Rh thermocouple as close as possible Fig. 4.

2. Procedure

With the apparatus assembled, helium was started through the tube to flush out air and moisture. The furnace was turned on and slowly brought up to the reaction temperature within one hour. The reactant gas was then started and the helium turned off. The temperature and gas flow were held for three hours at the end of which time the furnace was shut off, opened, the reactant gas stopped, and helium started again through the tube. The prism was removed and the tube was cleaned. Reactions were carried out at 200, 500, and 700° C. Above 700° C, the prisms would start to deform because of the amount of liquid phase present.

Any products formed, usually in very small amounts, were X-rayed to determine their identity. The reacted prisms were mounted in bakelite, sawed in half, and then polished. By examination under the metallographic microscope, the extent of the reaction could be visually determined.

3. Results

The gases tried in this preliminary work were: Oxygen (O_2), Hydrogen sulfide (H_2S), Methyl mercaptan (CH_3SH), Sulfur dioxide (SO_2), Sulfur hexafluoride (SF_6), Carbon dioxide (CO_2), Nitrogen dioxide (NO_2), Ammonia (NH_3), Methyl chloride (CH_4Cl), Ethyl chloride (C_2H_5Cl), Vinyl chloride
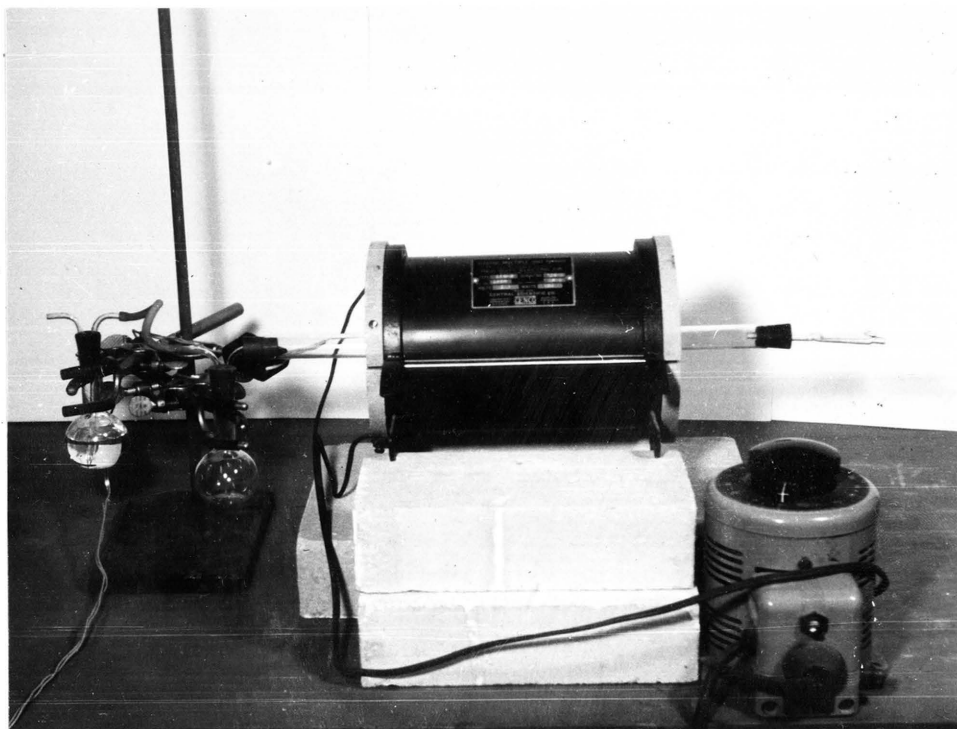
Figure 3   Apparatus Used for Preliminary
Investigations
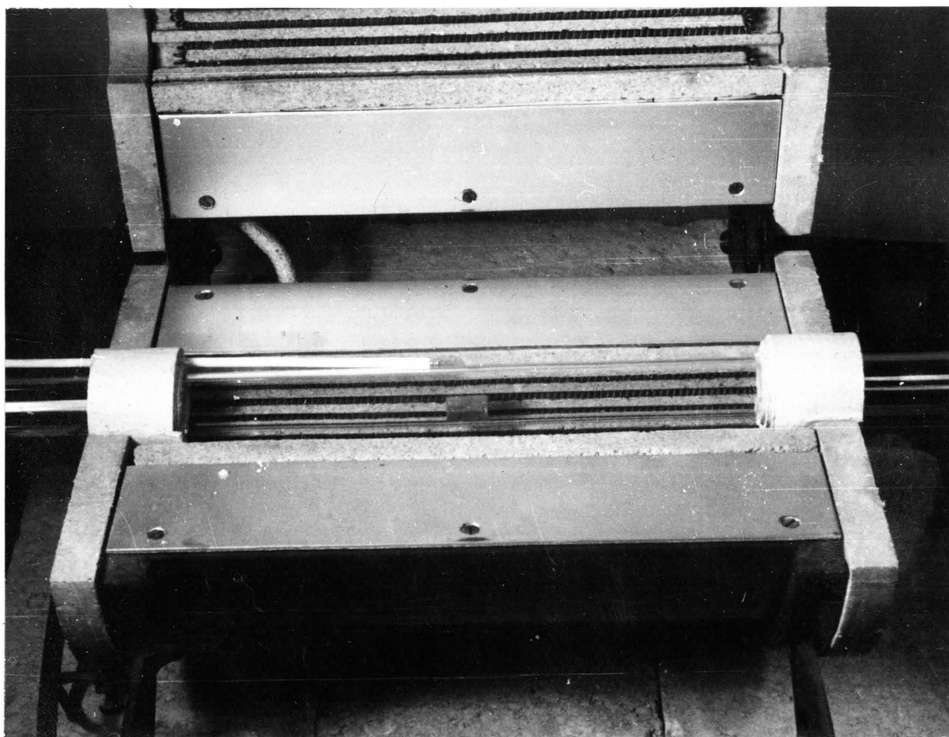
Figure 4   Alloy Prism Arranged in Tube Furnace

(C_2H_3Cl), Chlorine (Cl_2), Tri-methyl amine $(CH_3)_3N$, and Phosgene $(COCl_2)$.

Of all the gases tried, only chlorine gave a reaction at 200° C and at this temperature it completely consumed the prism. Carbon dioxide was the only gas that did not react at all at any of the temperatures. All of the other gases reacted to some extent at 500° C and 700° C.

The reactions of the alloy with hydrogen sulfide and methyl mercaptan were similar. No condensate containing tin or iron was formed. With hydrogen sulfide, a yellow condensate formed which was identified as sulfur and with methyl mercaptan, a reddish viscous liquid formed which is believed to be carbon subsulfide. From metallographic examination, the blocks appeared to be changed and a new product formed. By X-ray analysis, some extra lines showed up, but no conclusive evidence could be obtained. The lines for $FeSn_2$ were identified so it is evident that the reaction did not alter the prism completely.

The reaction of the alloy with oxygen and sulfur dioxide was similar in that they affected only the edge of the prism for a depth of not more than .03mm. Only the reaction with sulfur dioxide gave a condensate an it was identified as sulfur. The material formed on the prism edge by sulfur dioxide did not give a good X-ray pattern so could not be identified. That formed from oxygen was identified as Fe_2O_3 but the pattern was also poor. Some tin oxides may have been present.

The reaction of the alloy with nitrogen dioxide was only significant at 700° C. Two prisms were tried and different results were obtained each time. The first reaction produced a voluminous scale which filled the cross-section of the tube near the specimen, and produced a white condensate which contained tin. The X-ray analysis of the scale showed it to contain SnO_2. Many other lines were present which belonged to no listed compound. The second prism reacted under presumably the same conditions, and gave a tightly adherent scale which from X-ray analysis was SnO_2 and Fe_3O_4.

The reaction of the alloy with sulfur hexafluoride nearly consumed the prism at 500° C and did consume the prism at 700° C. The products which consisted of a condensate and residue could not be identified by X-ray diffraction. A gelatinous precipitate, formed in the water bubbler, contained no tin as analyzed by microchemical analysis.

The organic chlorides, methyl, ethyl, and vinyl gave condensates at 500° C and 700° C. All of the condensate appeared to have similar X-ray patterns which would lead one to believe that the same compound was produced regardless of what organic chloride was used. No diffraction data are available to identify the compound or compounds formed. The reactions seemed to progress better at 500° C than 700° C due to the decomposition of the organic material to give carbon at higher temperature. Not enough material was condensed so that it could be analyzed for iron or tin chemically.

At 500° C, using tri-methyl amine, the prism expanded, became porous, and gained in weight. A colorless but viscous liquid formed and condensed in the cool portion of the tube. At 700° C, the same as above happened, but instead of the prism becoming porous, a hard layer formed from the edge to about 0.5mm toward the center. The layer was sufficiently hard to make it difficult to saw with a hacksaw.

A layer formed around the prism when reacted with ammonia at 700° C. This layer was irregular but averaged about 0.5mm in thickness. X-ray diffraction showed it to be tin. At 500° C the prism just became porous. No condensates were found at either temperature.

At 500° C phosgene reacted almost completely with the prism converting the iron to $FeCl_2$ which remained behind as white tabular crystals. Some $FeCl_3$ formed which distilled over with the $SnCl_4$. At 700° C the iron was all converted to $FeCl_3$ which distilled over with the $SnCl_4$.

C. QUANTITATIVE INVESTIGATIONS

From the preliminary investigation, the reactions using phosgene and those using the organic chlorides showed the most promise. Further investigations were carried out to determine the quantitative effect these gases had on the removal of both the tin and the iron from the alloy.

1. Equipment

The apparatus which was used is pictured in Fig. 5. The reaction tube is a one and one quarter inch fused silica

tube closed at one end. It was heated by a 2575 watt resistance furnace manufactured by the Hevi Duty Electric Co. The temperature was measured with a 10% Pt-Rh thermocouple placed against the outside of the tube 2 1/4 inches from the closed end. Under static conditions, the inside temperature of various points was correlated with the temperature indicated by the outside thermocouple. The boat with the alloy was arranged as pictured in Fig. 6, the center of the boat being at the point of maximum temperature. The tube above the boat in Fig. 6 carry the gases into the reaction tube. It was also of fused silica and was supported by a "V" shaped silica rod welded to this tube. The outgoing unreacted gases plus gaseous reaction products were carried to an inverted 500ml flask by means of glass tubing connected together with short lengths of 1/4 inch tygon tubing. To allow any heavy vapors to condense or fine solid particles to be trapped, the gases were admitted with a tube about two inches long and exhausted through a tube which reached the bottom of the 500ml flask. These exhausted gases were then passed through a sintered glass disperser below the surface of distilled water held in a 500ml vacuum filtering flask.

The volume of the gases used was measured with "tri-flat" flowrators and "Fisher" flowrators.

2. Procedure

Approximately 20 grams of alloy were weighed into a silica boat of known weight. This boat containing the alloy was placed in the reaction tube which had been removed from
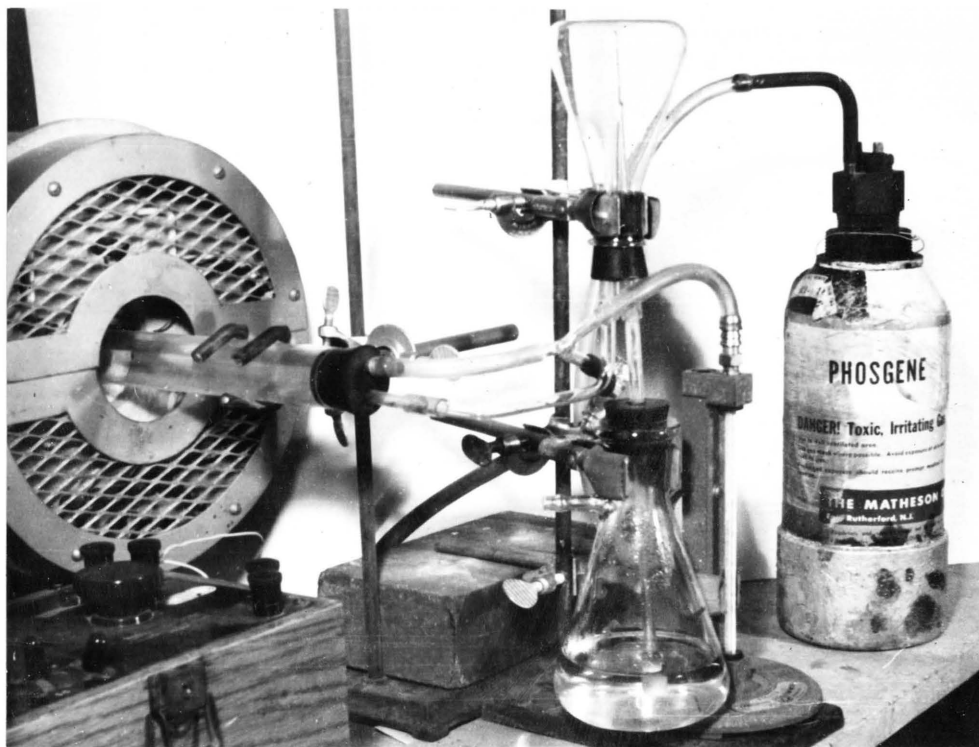
Figure 5   Apparatus for the Quantitative
Investigations
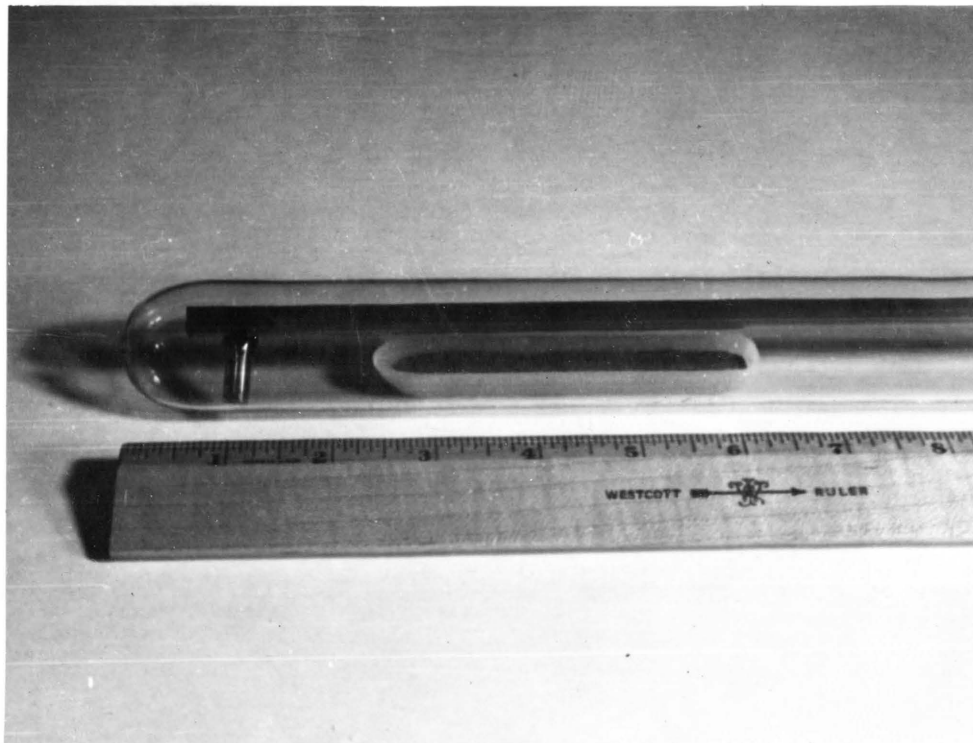
Figure 6   Placement of Silica Boat in Tube

the furnace. The stopper fitted with the two tubes was put on the reaction tube and sealed with rubber tape. Helium was circulated through the apparatus to remove the air after which the reaction tube was inserted into the hot furnace, and held at approximately the reaction temperature. When the desired temperature had been stabilized, the helium was shut off and the reactant gas or gases were passed over the alloy shot in the boat. After a predetermined volume of the reactant gas had passed over the alloy, the reactant gas was turned off, and helium was passed through the apparatus. The reaction tube was then withdrawn from the furnace to cool. When the apparatus had cooled, the boat was removed from the reaction tube, weighed, and the contents of the boat ground and analyzed for iron, tin, and chlorine. Any condensate formed was either washed or scraped from the tube and also analyzed for iron, tin, and chlorine. The solution from the scrubber was also analyzed for iron, tin, and chlorine.

3. Results

a. Organic Chloride Gases:

(1) Methyl Chloride

The effect of temperature on the removal of tin was studied for methyl chloride. The reaction time was three hours and the gas rate was such as to allow enough methyl chloride to pass over the alloy to convert all the tin to dimethyl tin dichloride. Table I shows the results from the experiments.

Most of the condensate was in the form of colorless needles extending the diameter of the tube. The balance was a white finely divided powder. From a melting point determination (106-107° C) and physical appearance of the crystals, they were identified to be dimethyl tin dichloride. No iron was found in the condensate and the maximum amount in the scrubber was .014 grams per liter or a total of .0035 grams.

(2) Ethyl Chloride

The effect of temperature on the removal of tin was studied for ethyl chloride. The reaction time was three hours and the rate was such as to allow enough ethyl chloride to pass over the alloy to convert all the tin to di-ethyl tin dichloride. Table II shows the results of the experiments. The tin compound partially condensed as a yellow liquid just inside the furnace. This yellow liquid turned into a white crystalline solid upon cooling. The other part condensed as a white finely divided powder on the bottom of the reaction tube.

From calculations using the analysis of the condensate, more tin was in the condensate than tin removed from the alloy. Even though a certain percent of iron was removed, none was recovered in either the condensate or the scrubber. The maximum amount of iron reported in the scrubber was .0018 grams and for the condensate none could be found.

TABLE I

Reaction of Methyl Chloride with the Iron Tin Alloy

Temp. of Reaction	% Sn Removed	% Fe Removed	% Sn in Condensate	% Sn rec. In Scrubber	% Sn rec. In Condensate
300	2.27	3.28	-	11.16	-
350	16.51	5.26	36.40	9.96	17.46
400	42.22	8.93	41.20	3.04	47.4
450	32.22	7.79	35.85	0.95	37.8
500	34.07	10.01	72.36	2.56	100.0 +

TABLE II

Reaction of Ethyl Chloride with the Iron Tin Alloy

Temp. °C	% Sn Removed	% Fe Removed
400	11.9	7.63
450	23.8	9.61
500	27.2	9.35

TABLE III

Reaction of Vinyl Chloride with the Iron Tin Alloys

Temp. °C	% Sn Removed	% Fe Removed
350	0.58	0.0
400	-	0.0
450	15.02	0.0
500	19.60	0.0

TABLE IV

Reaction of Phosgene with the Iron-Tin Alloy

Temp. °C	% Sn Removed	% Fe Removed
400	4.85	0.96
425	10.67	1.96
450	28.49	7.5
475	37.57	29.1

(3) Vinyl Chloride

The effect of temperature on the removal of tin was studied for vinyl chloride. The flow rate of the vinyl chloride was such as to have sufficient vinyl chloride to convert all the tin to a divinyl tin dichloride analogous to the diethyl and dimethyl tin dichlorides. Since in the previous reactions the analyses of the condensates were not trustworthy, just the residues were analyzed. The results of the experiments are given in Table III.

The condensate had the same appearance as the condensate in the reaction with ethyl chloride. According to the iron analyses, more iron was present after the reaction than before; however, the error lies within 2%.

b. Phosgene and Mixtures of Carbon Monoxide and Chlorine:

(1) Phosgene

The reactions between phosgene and the iron-tin alloy shot were studied quantitatively at various temperatures. The volume of phosgene used was calculated on the basis of converting all of the tin to tin tetrachloride and the iron to ferrous chloride. The phosgene was passed over the alloy for three hours. A separation was based on the fact that at the temperature of operation, the tin tetrachloride formed is a gas and the ferrous chloride, a solid with no appreciable vapor pressure. If any ferric chloride would form, however, it would distill off with the tin tetrachloride for it has a high vapor pressure at elevated temperatures. In order to keep the tin from being contaminated with iron, it is neces-

sary to prevent this ferric chloride from forming. By the experiments performed, it was found that adding carbon monoxide to the phosgene helped in preventing this iron contamination of the condensate. The results obtained are listed in Table IV. At $450^{\circ}C$, some ferric chloride formed in the tube and at $475^{\circ}C$, the crystals of ferric chloride extended across the diameter of the reaction tube.

(2) Carbon Monoxide and Chlorine

Since carbon monoxide and chlorine will combine readily to form phosgene, it was thought that a mixture of the two gases would then produce the same effect as phosgene did. The optimum temperature of $450^{\circ}C$ was chosen and a gas volume sufficient to convert all of the tin to tin tetrachloride and the iron to ferrous chloride was employed. The volume of gas was passed over the alloy for three hours. The data obtained are in Table V.

In all the reactions, sufficient ferric chloride formed so that the crystals extended across the diameter of the reaction tube. It was believed that some free chlorine existed which was causing the iron to be converted to ferric and not ferrous chloride.

(3) Carbon Monoxide and Phosgene

To eliminate the possibility of having free chlorine present to react with the alloy, mixtures of carbon monoxide and phosgene were tried. The reactions again lasted three hours and sufficient phosgene was used so that all of the tin could be converted to tin tetrachloride and the iron to

ferrous chloride. Table VI gives the results of the experiments.

For the first two hours and fifteen minutes, very little ferric chloride formed. It was only during the last fifteen minutes that most of it formed. Much less ferric chloride formed while using mixtures of carbon monoxide and phosgene than when using carbon monoxide and chlorine.

(4) Appearance of Boat After Reaction

In all of the reactions incorporating carbon monoxide and chlorine, phosgene, or carbon monoxide and phosgene, the appearance of the boat was the same. A layer of off-white plate-like crystals formed on top for about one-eighth of an inch. Under this layer, the alloy was cemented together by a water soluble reaction product. The top layer of crystals, a sample from the bottom, and a sample from the middle of the charge were analyzed and the results tabulated in Table VII.

The top layer was identified as unreacted alloy mixed with crystals of ferrous chloride and stannous chloride. The plate-like crystals were ferrous chloride, and the stannous chloride in solution with ferrous chloride was the water soluble compound holding the alloy shot together. The ferrous chloride crystals were qualitatively checked for tin and none was found.

D. FURTHER INVESTIGATIONS WITH PHOSGENE, CHLORINE, AND CARBON MONOXIDE

From the previously obtained data, the reactions with

TABLE V

Reaction of Carbon Monoxide and Chlorine with the Iron-Tin Alloy at 450°C

Ratio $CO : Cl_2$	% Sn Removed	% Fe Removed
1:1	23.12	65.37
2:1	58.97	57.98
3:1	64.53	52.95

TABLE VI

Reaction of Carbon Monoxide and Phosgene with the Iron-Tin Alloy

Temp. °C	Ratio $COCl_2$:CO	% Sn Removed	% Fe Removed
450	2:1	29.38	4.15
475	2:1	82.63	?
475	1:1	34.89	24.59
475	1:2	53.26	?
500	1:2	48.61	18.54
500	1:3	58.09	30.36

TABLE VII

Tin and Iron Distribution in Silica Boat After Reaction

	Total %		H_2O Sol.		% Cl
	% Sn	% Fe	% Sn	% Fe	
Top 1/8 inch	13.94	36.11	11.44	29.77	28.68
Middle sample	54.44	20.74	11.95	8.45	14.91
Bottom Sample	57.44	19.09	2.85	7.40	9.86
Orig. alloy	72.91	26.45	-	-	-

phosgene and carbon monoxide appeared to be most promising, first because of the larger amount of tin removed by them and secondly the relative cost as compared with the organic chloride gases. It is for these reasons that a further study of the reactions with phosgene and carbon monoxide were continued and further investigation of the organic chloride reactions abandoned.

1. Description of Apparatus

To obtain higher removal of tin, better gas solid contact was sought. To accomplish this, alloy shot was supported in the center of a 10mm pyrex tube by means of pyrex wool as shown in Fig. 7. The alloy in the tube was placed in the center of a wire wound resistance furnace. The thermocouple junction was placed against the outside of the tube at the center of the alloy. An empty tube was substituted for a tube containing the alloy and was positioned in the furnace in the same way as those tubes containing alloy. The outside thermocouple was placed at the mid-point of the tube. With the temperature of the furnace as measured by the outside thermocouple held constant, the temperature gradient in the tube was measured with another thermocouple. From the data obtained the temperature of the alloy could be measured, knowing the furnace temperature.

Tri-flat flowrators were used to measure the gases. The gases were mixed in a glass "Y" just before entering the furnace. The overall view of the apparatus is pictured in Fig. 8. The gases after leaving the 10mm tube went into a 500ml
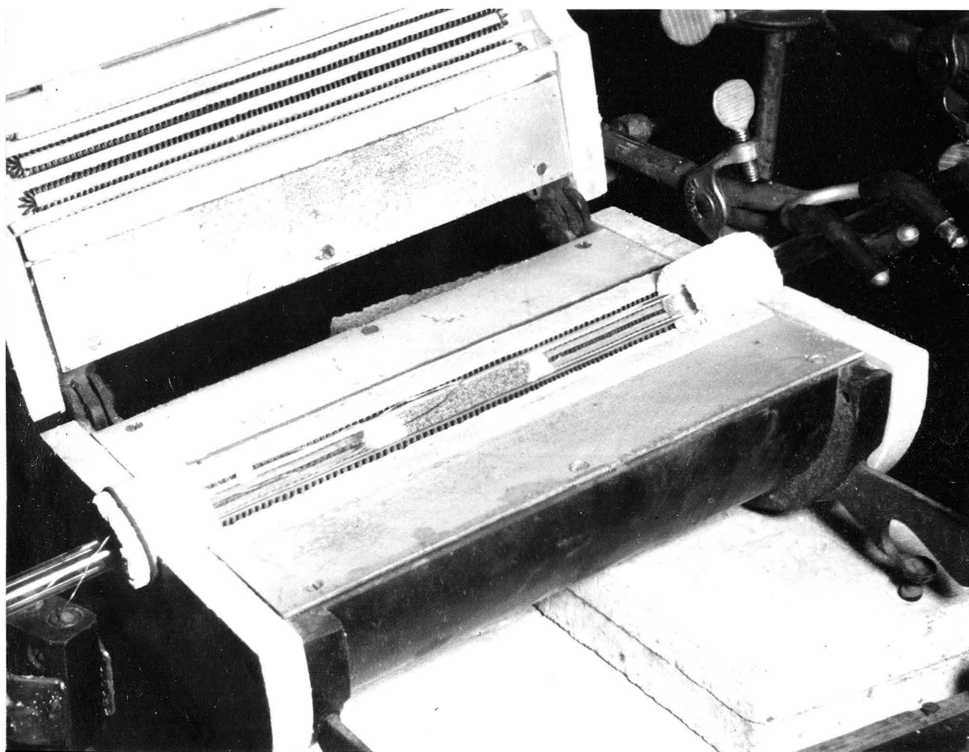
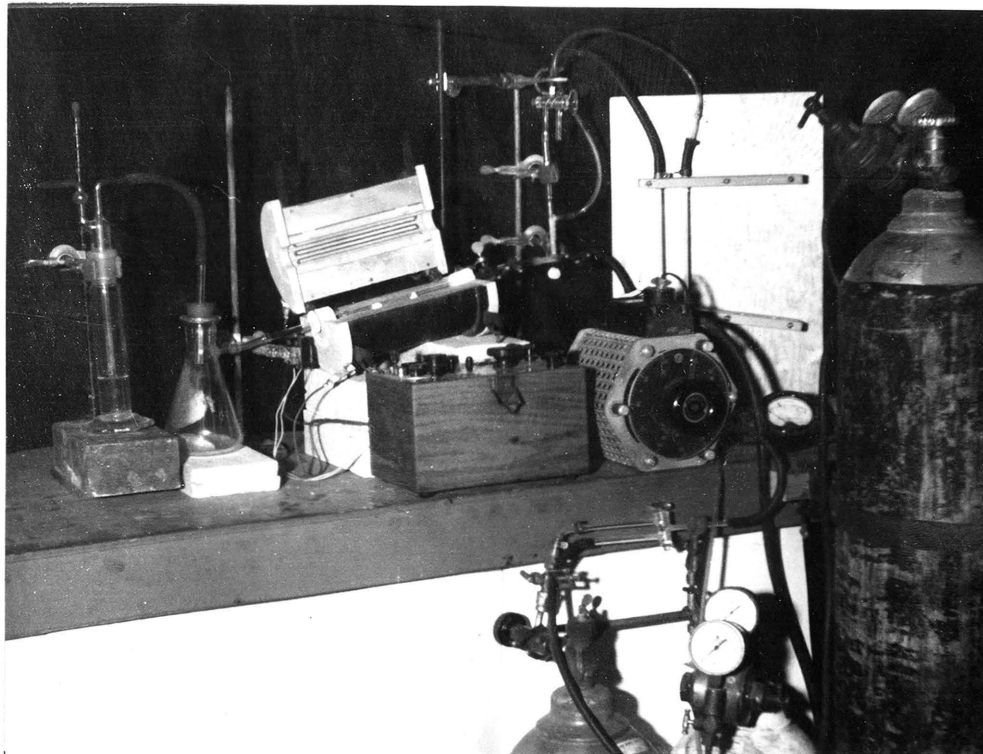Figure 7   Placement of Alloy Shot in
10mm. Glass Tube

Figure 8   Apparatus for Reacting the Gases With
the Alloy in the 10mm. Glass Tube

vacuum filtering flask and then through a water trap. After a few experiments, it was found better to incline the 10mm tube and furnace at an angle of about 15° to the horizontal. Two two-way valves were placed in the chlorine and phosgene line, one before and one after the flowrator so the flowrator could be flushed out with helium after use to prevent it from sticking.

2. Procedure

The 10mm tube containing the alloy at the midpoint was placed in the furnace and the thermocouple positioned. Helium was circulated through the tube a few minutes before the furnace was turned on and kept circulating until the alloy was at the desired reaction temperature. The helium was then stopped and the reactant gases were started through the alloy. At the end of the reaction, the reactant gases were turned off and helium was again circulated through the apparatus while it was cooling down. When cool, the 10mm tube was removed from the furnace and cut on each side of the charge just past the pyrex fiber. The tube was then placed in about 250m. of distilled water to which 5ml of concentrated hydrochloric acid was added. The hydrochloric acid partially prevented the tin salts from hydrolyzing. The concentration of the acid was not sufficient to attack any of the alloy. The alloy was filtered from this solution and then dissolved in concentrated hydrochloric acid after which this alloy solution was filtered to remove the glass fibers. Both solutions were diluted to 250ml in volumetric

flasks and analyzed for tin and iron.

3. Results

The results obtained are tabulated in Table VIII. It was
expected that phosgene would react with the alloy in the tube
the same way that it did when the alloy was placed in the
boat but to a greater extent since there was better gas-
solid contact in the tube. In reactions I, II, III, and IV,
the temperature and total gas was the same as that used in
the reactions of the alloy in the silica boat. The products
of the reaction, however, were not the same. With those
reactions of the alloy in the boat, tin tetrachloride formed.
None formed, however, when the alloy was in the tube. The
tubes also clogged after the reaction had been under way only
a short time. Unclogging of the tubes was made possible by
heating them above $580^{\circ}C$ with a helium atmosphere. When the
plug in the tube broke through, a white material deposited
in the cool portion of the tube and a light yellow liquid
condensed in the hotter portion of the tube. This liquid
became a white solid upon cooling. Both the liquid and the
white material were identified as anhydrous stannous chloride.

Two reactions (V and VI) with phosgene were tried at a
higher temperature to try to prevent this clogging. When
the reaction was started stannous chloride distilled over and
condensed in the cooler portion of the tube. Toward the end
of the reaction there was a sudden increase in temperature
and a brownish liquid formed just past the fiber plug. It
crystalized into a light brown solid. Qualitative tests
showed this material to contain iron. Some alloy still

TABLE VIII

Results of Reactions Carried Out In 10mm. Glass Tube

React.	Alloy ^oC Temp.	Gas Rate *ml/min.*			React. Time	Metal Removed		Remaining Alloy % Sn
		$COCl_2$	CO	Cl_2		% Sn	% Fe	
V	609-654	63.3	–	–	1 hr.	63.82	9.35	55.3
IV	454	63.5	–	–	approx. 1 hr.	5.77	0	72.18
III	424	63.5	–	–	1.5 hrs.	3.43	0	77.94
II	404	63.5	–	–	2 hrs.	2.19	0	76.16
I	404	63.5	–	–	1 hr.	1.64	0	75.22
VI	609	63.3	–	–	1 hr.	64.56	3.9	59.06
X1II	609	63.3	63.3	–	1 hr.	76.37	0	56.82
XII	609	63.3	63.3	–	1 hr.	47.93	0	63.42
XI	609	21.1	105.5	–	4 hr.	58.24	0	63.50

TABLE VIII CONTINUED

Results of Reactions Carried Out In 10mm. Glass Tube

React.	Alloy °C Temp.	Gas Rate ml./min.			React. Time		Metal Removed		Remaining Alloy % Sn
		COCl$_2$	CO	Cl$_2$			% Sn	% Fe	
X	609	21.1	105.5	-	3	hrs.	66.07	0	61.09
IX	579	31.5	156.5	-	1.5	hrs.	33.65	0	69.01
VIII	579	21.1	105.5	-	2	hrs.	33.10	0	68.12
VII	594	21.1	105.5	-	1 hr. 43 min.		28.5	0	70.46
XIV	609	-	64.3	31.7	1 hr. 23 min.		96.56	31	24.64
XV	609-654	-	126.8	31.7	53	min.	92.3	47	37.4
XVI	609	-	126.8	31.7	15	min.	34.89	0	63.9
XVII	609	-	126.8	31.7	30	min.	42.99	0	60.9
XVIII	609	-	126.8	31.7	54	min.	70.19	0	47.8

remained in the tube after both reactions.

To try to prevent iron from contaminating the condensate, mixtures of carbon monoxide and phosgene were tried (VII, VIII, IX, X, XI, XII, XIII). In all cases stannous chloride was produced free of iron. According to analysis no iron was removed from between the fiber plugs. In all the reactions up to XIII the furnace was horizontal. For reaction XIII, the furnace was inclined at an angle of about 15° to the horizontal to allow the stannous chloride to be removed. The furnace was kept this way for the balance of the reactions. By comparing reactions XII and XIII, it can be seen that inclining the furnace helps to remove the tin from the iron.

Since phosgene would be too expensive for a commercial process, mixtures of carbon monoxide and chlorine were tried. In reactions XIV and XV, stannous chloride formed without any indication of being contaminated with iron until the very end of the reaction. At that time ferric chloride started distilling over and discolored the stannous chloride. Three reactions (XVI, XVII, XVIII) were tried in which the gas rate and temperature were held constant and the time of the reaction was varied. No iron was removed in any of the above reaction times. In all cases, there was still some remaining alloy the composition of which was decreasing in the percent tin.

4. Reaction of Carbon Monoxide - Chlorine Mixtures with Ferrous Chloride

Anhydrous ferrous chloride was substituted for the alloy in the 10mm. glass tube. It was heated in a helium atmosphere

to 610°C and 680°C. At a gas ratio (carbon monoxide to chlorine) of 160/1, it was possible to prevent ferrous chloride from converting to ferric chloride. The reaction was exceedingly sensitive to changes of the gas ratio and somewhat sensitive to temperature changes. With the equipment available, it was impossible to obtain more accurate data.

IV THEORY OF THE PHOSGENE REACTIONS

A. PROPERTIES OF THE REACTANTS AND PRODUCTS

The melting point, boiling point, specific gravity and atomic weights of tin, iron, phosgene, stannous chloride, ferrous chloride, ferric chloride, and stannic chloride are tabulated in Table IX. The vapor pressures of the above chlorides at different temperatures are listed in Table X and plotted in Fig. 10.

Below $319^{\circ}C$ ferric chloride [59] has the formula $FeCl_3$ but above this temperature as a gas it changes to Fe_2Cl_6.

(59) Hodgman, M. S., Charles D., Handbook of Chemistry and Physics, 13th edit., Chemical Rubber Publishing Co., Cleveland, Ohio.

Muromtsev and Nazarova [66] found the vapor pressure of stannous chloride and ferrous chloride above salt mixtures of the two compounds at a temperature of $550^{\circ}C$ by passing a stream of air over the molten mixture. The results are tabulated in Table XI. Beyond 45 weight percent ferrous chloride, the salt mixture becomes hetergeneous, part of the ferrous chloride going over into solid at $550^{\circ}C$. In the ferrous chloride-stannous chloride system, the partial pressure of the components are very widely divergent and azeotropy is absent; this makes separation by distillation possible.

(66) Muromtsev, B. A., and Nazarova, L. A., Vapor Pressure and Composition in the Binary Mixtures $PbCl_2 + ZnCl_2$ and $SnCl_2 + FeCl_2$, J. Gen. Chem. U.S.S.R. 16, 1767 (1946)

TABLE IX

Properties of Products and Reactants from Phosgene Reactions

Substance	Melting Point[59]	Boiling Point[59]	Specific Gravity[64]	Atomic Weight[64]	Description[64]
Sn	$231.9^{\circ}C$	$2337^{\circ}C$	7.28	118.70	white metal
Fe	$1535\ ^{\circ}C$	$3073^{\circ}C$	7.86	55.84	silvery metal
$COCl_2$	$-118\ ^{\circ}C$	$8.3^{\circ}C$	-	98.92	gas
$SnCl_2$	$247\ ^{\circ}C$	$623^{\circ}C$	$3.393^{245^{\circ}C}$	189.61	crystaline white
$FeCl_2$	$677\ ^{\circ}C$	$1026^{\circ}C$	2.98	126.75	green to yellow crystals
$FeCl_3$	$319\ ^{\circ}C*$	-	2.804	162.21	black-brown crystals
$SnCl_4$	$-33.3^{\circ}C$	$113^{\circ}C$	2.232	260.53	colorless liquid

(59) Data taken from Selected Values of Chemical Thermodynamic Properties, Circular 500, National Bureau of Standards, except for that of $COCl_2$ - see reference (64) below.
(64) Data taken from Handbook of Chemistry and Physics, 13th edit., Chemical Rubber Publishing Co.

*Sublimes to Fe_2Cl_6 at $319^{\circ}C$

TABLE X

Temperature – Vapor Pressure of the Chlorides[62]

Vapor Pressure mm.	.076	.76	7.6	76	190	380	760
Compound							
$FeCl_2$ (l)	–	–	–	822	893	956	1026
Fe_2Cl_6 (s)	172	189	230	267	283	297	–
$SnCl_2$ (l)	250	308	381	479	531	574	623
$SnCl_4$ (l)	–	-26	5.5	48.5	70	90.5	113

(62) Data Taken from Kelley, K. K., Contributions to the Data on Theoretical Metallurgy, IV, The Free Energies of Vaporization and Vapor Pressures of Inorganic Substances, Bull. 383, U. S. Bureau of Mines
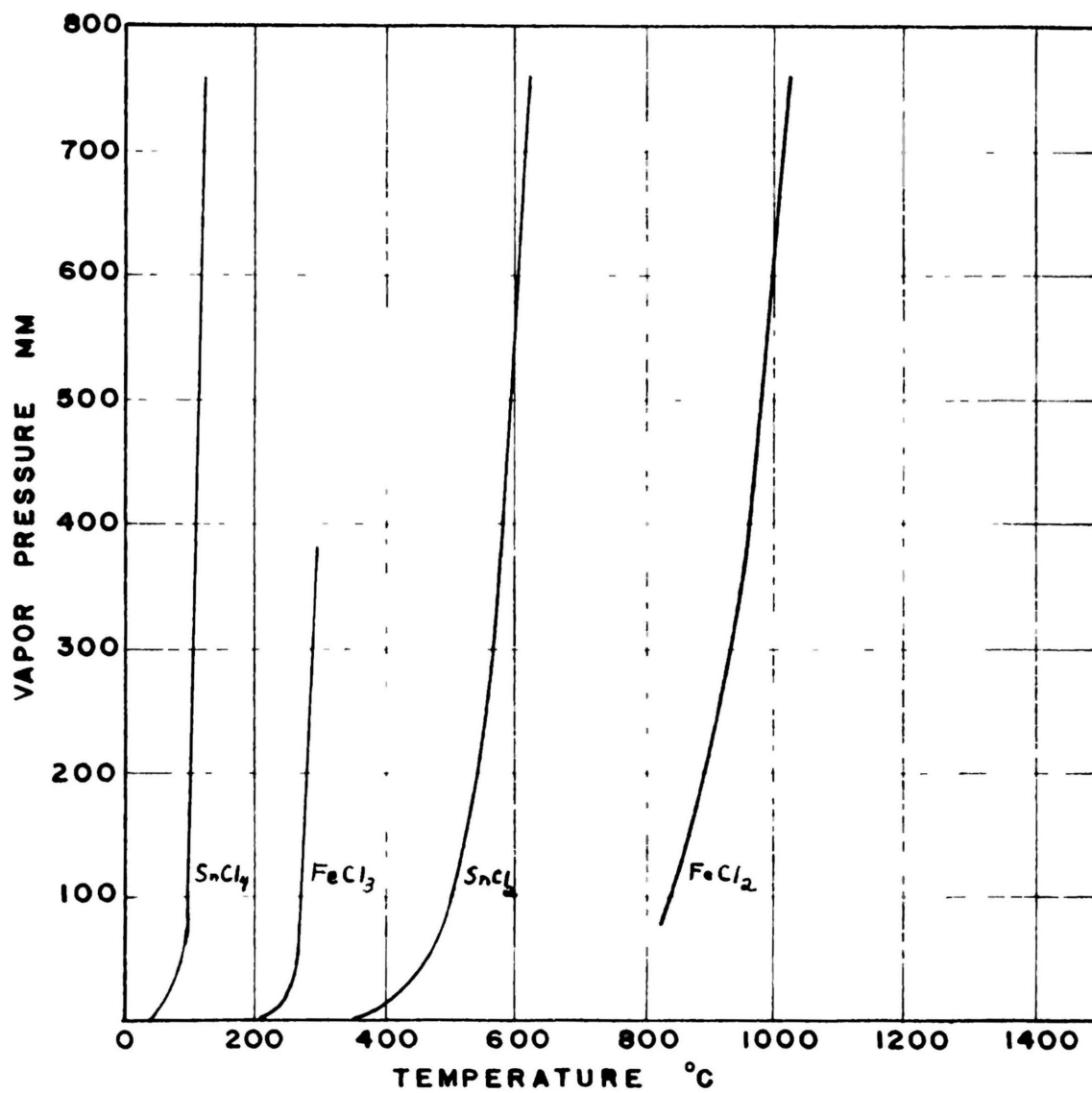
Figure 9. Variation of the vapor pressure with
temperature for the chlorides.

TABLE XI

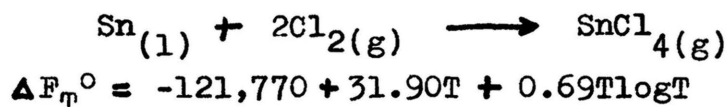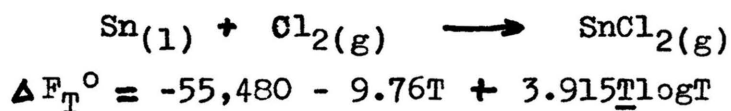Vapor Pressure of $SnCl_2$ and $FeCl_6$ Above Their Molten Salt Mixture at 550°C (66)

Composition of liquid mole % Sn	Composition of vapor mole % Sn	Partial Pressures mm.	
		$SnCl_2$	$FeCl_2$
84.21	98.81	267	3.3
56.82	72.26	164	4.8
45.19	93.13	133	8.3

(66) Muromtsev, B. A., & Nazarova, L. A., Vapor Pressure and Composition in the Binary Mixtures $PbCl_2$ + $ZnCl_2$ and $SnCl_2$ + $FeCl_2$, J. Gen. Chem. U.S.S.R. 16, pp. 1767-76 (1946)

B. THERMODYNAMICS OF PRODUCTS AND REACTANTS

The standard free energy equations of formation of, ferrous chloride, stannous chloride, and stannic chloride were obtained from Kellogg's [58] data and are listed as follows:

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(58) Kellogg, Herbert H., Thermodynamic Relationships in Chlorine Metallurgy, Journal of Metals, Transactions AIME, Vol. 188, oo. 862-872, June, 1950.

$$Fe_{(s)} + Cl_{2(g)} \longrightarrow FeCl_{2(s)}$$
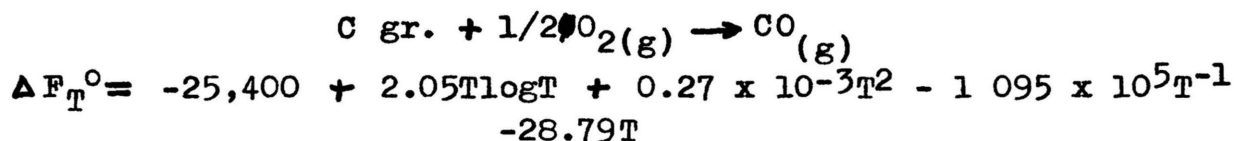$$\Delta F_T^\circ = -82,800 + 57.90T + 0.59 \times 10^{-3}T^2 - 9.21T\log T + 0.245 \times 10^5 T^{-1}$$

$$Fe_{(s)} + Cl_{2(g)} \longrightarrow FeCl_{2(1)}$$
$$\Delta F_T^\circ = -74,750 + 62.63T - 13.45T\log T$$

$$Sn_{(1)} + Cl_{2(g)} \longrightarrow SnCl_{2(1)}$$
$$\Delta F_T^\circ = -85,800 + 94.76T - 20.04T\log T$$

$$Sn_{(1)} + Cl_{2(g)} \longrightarrow SnCl_{2(g)}$$
$$\Delta F_T^\circ = -55,480 - 9.76T + 3.915T\log T$$

$$Sn_{(1)} + 2Cl_{2(g)} \longrightarrow SnCl_{4(g)}$$
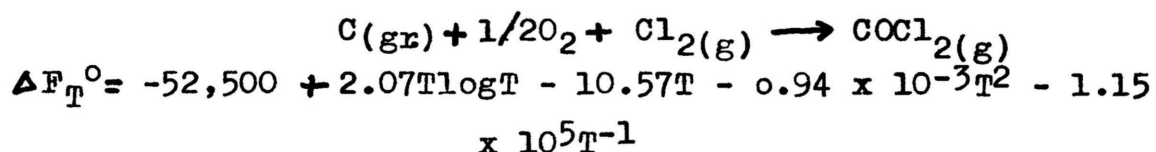$$\Delta F_T^\circ = -121,770 + 31.90T + 0.69T\log T$$
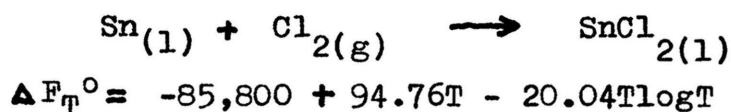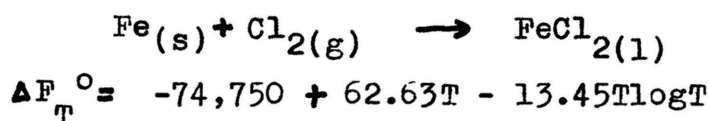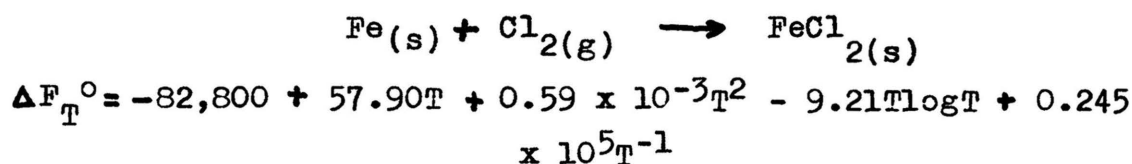
The standard free energy equation of formation of carbon monoxide was obtained from Coughlin [60] and is as follows:

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(60) Coughlin, J. P., Contributions to the Data on Theoretical Metallurgy XII Heats and Free Energies of Formation of Inorganic Oxides, U. S. Bureau of Mines, No. 542.

$$C \text{ gr.} + 1/2O_{2(g)} \longrightarrow CO_{(g)}$$

$$\Delta F_T{}^\circ = -25,400 + 2.05T\log T + 0.27 \times 10^{-3}T^2 - 1\ 095 \times 10^5 T^{-1}$$
$$-28.79T$$

The standard free energy equation of formation of phosgene was calculated using the heat capacity equations of graphite, oxygen, chlorine, and phosgene from Kelley [63], the H at 298°A from Kubaschewski [61] and the entropies at 298°A from the National Bureau of Standards Circ. 500 [64]. The equation obtained is as follows:

$$C_{(gr)} + 1/2O_2 + Cl_{2(g)} \longrightarrow COCl_{2(g)}$$

$$\Delta F_T{}^\circ = -52,500 + 2.07T\log T - 10.57T - 0.94 \times 10^{-3}T^2 - 1.15$$
$$\times 10^5 T^{-1}$$

The standard free energy equation of formation of ferric chloride was calculated from the data in the tables of Kubaschewski [61] and is as follows:

$$2Fe_{(s)} + 3Cl_2 \longrightarrow Fe_2Cl_{6(g)}$$

$$\Delta F_T{}^\circ = -155,950 + 23.8T$$

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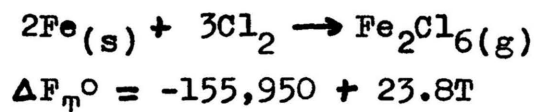
(63) Kelley, K. K., Contributions to the Data on Theoretical Metallurgy High-Temperature Heat-Content, Heat-Capacity, and Entropy Data for Inorganic Compounds, Bull. 476.
(61) Kubaschewski, O., and Evans, E. Ll., Metallurgical Thermochemistry, New York Academic Press Inc., 1951.
(64) Selected Values of Chemical Thermodynamic Properties, National Bureau of Standards Circular 500.

The standard free energies from Osborn [65] were com-

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(65) Osborn, C. J., The Graphical Representation of Metallurgical Equilibria, Journal of Metals, Trans. AIME, Vol. 188, March, 1950.

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pared with those of Kubaschewski [61] and there was found to be a large discrepancy between them. For the reactions:
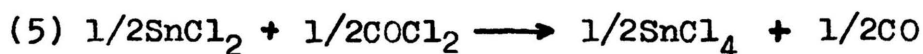
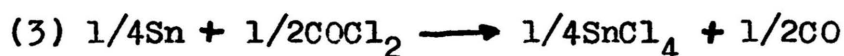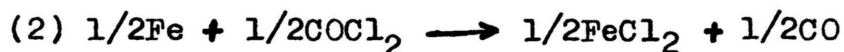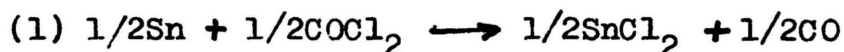$$Fe_2Cl_{6(g)} + Fe_{(s)} \longrightarrow 3FeCl_{2(s)}$$
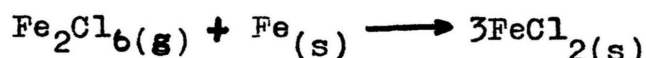
Using Osborn's data gives a standard free energy of reaction of +44.4 Kcal. whereas using the date of Kubaschewski gives a standard free energy of reaction to be -37.0 Kcal. Both calculations were made at a temperature of 500°C. In experiments performed where ferious chloride was heated in a stream of helium at the temperature of 500°C no decomposition of the ferrous chloride to ferric chloride and iron was noted. Therefore, on this evidence, it is unreasonable to believe that Osborn's data are correct, so Kubaschewski's data were used.

The values of the standard free energies are tabulated in Table XII.

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(61) Kubaschewski, O., and Evans, E. Ll., Metallurgical Thermochemistry, New York Academic Press Inc., 1951.

C. THERMODYNAMICS OF THE POSSIBLE REACTIONS

In the reaction of phosgene with the iron-tin alloy, all the possible reactions that might be encountered are listed below and on the following page:

(1) $1/2Sn + 1/2COCl_2 \longrightarrow 1/2SnCl_2 + 1/2CO$

(2) $1/2Fe + 1/2COCl_2 \longrightarrow 1/2FeCl_2 + 1/2CO$

(3) $1/4Sn + 1/2COCl_2 \longrightarrow 1/4SnCl_4 + 1/2CO$

(4) $1/3Fe + 1/2COCl_2 \longrightarrow 1/6Fe_2Cl_6 + 1/2CO$

(5) $1/2SnCl_2 + 1/2COCl_2 \longrightarrow 1/2SnCl_4 + 1/2CO$

$$(6) \quad 1/2CO + 1/2Cl_2 \longrightarrow 1/2COCl_2$$

$$(7) \quad 1/6Fe_2Cl_6 + 1/6Fe \longrightarrow 1/2FeCl_2$$

$$(8) \quad 1/6Fe_2Cl_6 + 1/6Sn \longrightarrow 1/6SnCl_2 + 1/3FeCl_2$$

$$(9) \quad 1/4SnCl_4 + 1/4Fe \longrightarrow 1/4FeCl_2 + 1/4SnCl_2$$

$$(10) \quad 1/4SnCl_4 + 1/4Sn \longrightarrow 1/2SnCl_2$$

$$(11) \quad FeCl_2 + 1/2COCl_2 \longrightarrow 1/2Fe_2Cl_6 + 1/2CO$$

$$(12) \quad 1/2FeCl_2 + 1/2Sn \longrightarrow 1/2SnCl_2 + Fe.$$

$$(13) \quad 1/3SnCl_4 + 2/3Fe \longrightarrow 1/3Fe_2Cl_6 + 1/2Sn$$

Using the data in Table XII the standard free energies
of these reactions were computed and the results tabulated
in Table XIII. By writing all of the equations so that one
gram atom of chlorine is being reacted in each equation, the
standard free energies of the reaction can be compared
directly. To do this, the data from Table XIII have been
plotted in Fig. 10. The equations whose standard free ener-
gies are the largest in the negative direction will take
place before those equations which are more positive. This
comparison can be made provided it is kept in mind that these
are standard free energies and both the products and reactants
of the equations must be in their standard states.

D. MECHANISM OF THE REACTION

When chlorine and carbon monoxide are brought together
and energized either by light or heat, they combine to form
phosgene. Fig. 10 shows that the formation of phosgene from
carbon monoxide and chlorine is negative. Therefore, it can
be assumed that the reactions in the tube primarily take place
with phosgene.

TABLE XII

STANDARD FREE ENERGIES OF COMPOUNDS II Kcal

Temp°C	400	500	600	700
Compound				
$SnCl_2$	−60.2	−57.3	−54.5	−53.6
$SnCl_4$	−99.0	−95.6	−92.2	−8?.7
$FeCl_2$	−61.1	−58.2	−55.4	−52.9
Fe_2Cl_6	−139.9	−137.6	−135.2	−132.8
$COCl_2$	−56.3	−56.8	−57.3	−57.8
CO	−40.9	−43.1	−45.2	−47.3

TABLE XIII

STANDARD FREE ENERGIES OF POSSIBLE REACTIONS WHEN USING
PHOSGENE IN Kcal

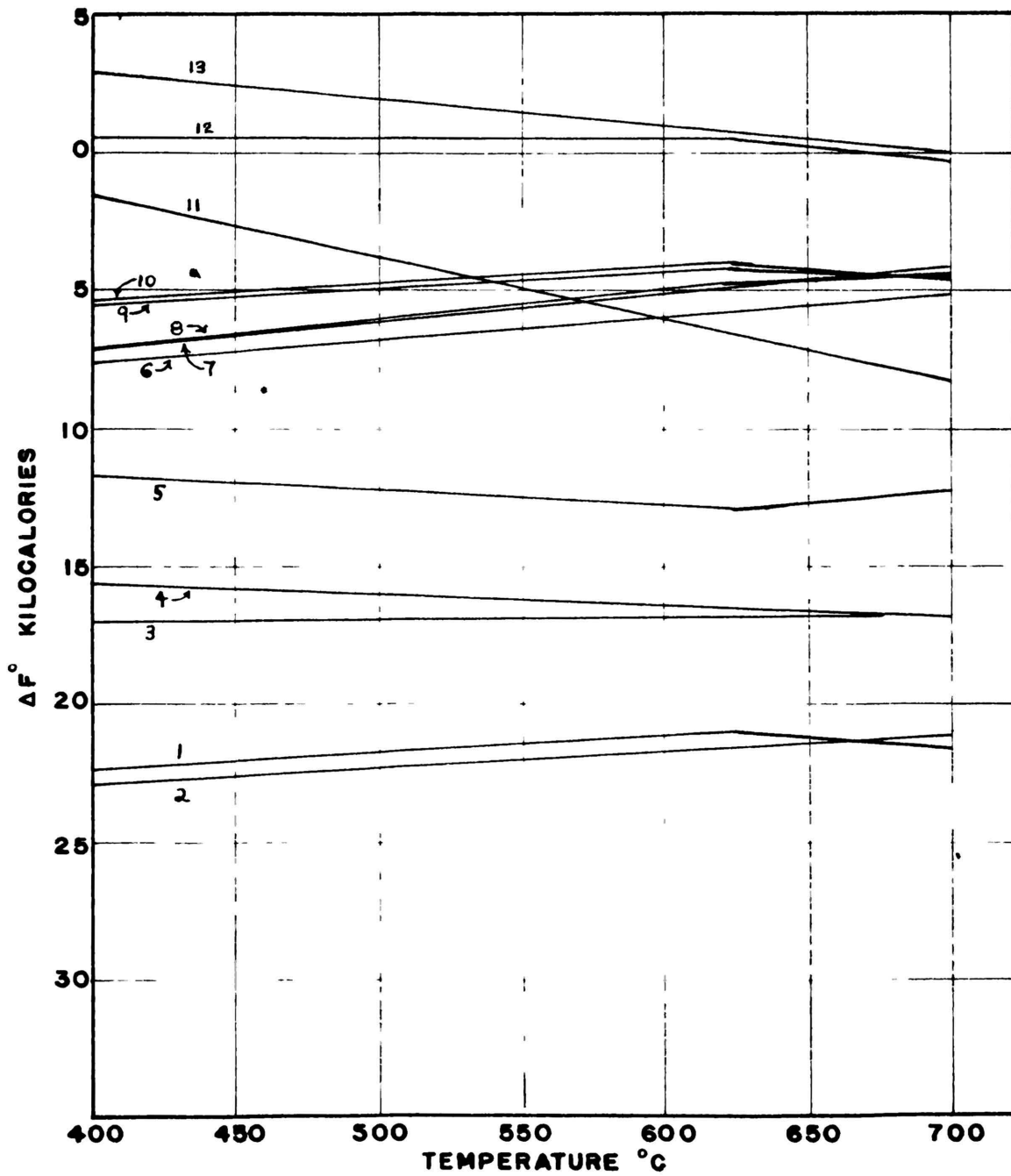| Temp°C	400	500	600	700
Reaction				
(1)	−22.4	−21.8	−21.2	−21.6
(2)	−22.9	−22.3	−21.7	−21.2
(3)	−17.1	−17.1	−17.0	−16.8
(4)	−15.6	−16.1	−16.5	−16.9
(5)	−11.7	−12.3	−12.8	−12.3
(6)	− 7.7	− 6.9	− 6.1	− 5.1
(7)	− 7.2	− 6.2	− 5.2	− 4.2
(8)	− 7.1	− 6.0	− 5.0	− 4.4
(9)	− 5.6	− 5.0	− 4.4	− 4.5
(10)	− 5.4	− 4.8	− 4.2	− 4.6
(11)	− 1.0	− 3.8	− 6.1	− 8.3
(12)	+ .45	+ .45	+ .45	− .35
(13)	+ 2.9	+ 1.9	+ 1.0	+ .08

Figure 10. Variation of the standard free energy with temperature for the possible reactions.

Phosgene first reacts with the iron tin alloys to form stannous and ferrous chlorides. If operating at a temperature above the boiling point of $SnCl_2$ ~~tin~~ and below the melting point of ferrous chloride, tin will be removed from the scene of the reaction immediately as a gas; whereas the iron will remain behind as ferrous chloride. This is evident by noting that the curves for these reactions in Fig. 10 are the most negative of all the curves. Since the ferrous chloride when formed is a solid, it surrounds the alloy shot so the gas can no longer get to the metal. The phosgene can however react with this ferrous chloride and convert it to ferric chloride which is a gas. This ferric chloride when it comes in contact with more alloy will be reduced back to ferrous chloride again. These reactions are shown to be possible by noting in Fig. 10 that their standard free energies are negative. It is also substantiated by the facts that with the reactions in the 10mm glass tube no iron was left as metallic iron or as ferrous chloride in the first part of the tube where the alloy had been placed and also that no ferric iron could be found as long as sufficient alloy remained in the tube for the reactant gases to pass through.

From Fig. 10 it can be also noted that it is not likely for the stannous chloride to react with the alloy to deposit tin for the free energy of the reaction is approximately zero; therefore, any of the stannous chloride formed will pass through the alloy without being reduced by the alloy.

The difference between the standard free energy of the
reaction of phosgene with iron and with tin is not very great;
therefore, one would ex ect that it would be just as easy to
chlorinate the tin as the iron. Likewise, the differences in
the standard free energy between the reaction of ferric
chloride and iron, and ferric chloride and tin is small so
one would expect that it would be easy to chlorinate either
the iron or the tin with the ferric chloride.

V CONCLUSIONS

From the investigations performed, it was found that mixtures of chlorine and carbon monoxide are the best gases of those investigated to separate iron from tin when these metals are associated together. The chlorination should be carried out between 625°C and 677°C. The products which form are stannous chloride of sufficient purity that if it were directly reduced it would produce salable tin, and ferrous chloride which would remain in the reactor.

It is believed that this process might eliminate the costly three or four step smelting process that is now employed in the refining of tin. A flowsheet that might utilize this chlorination process is as follows: The ore is smelted with limited reducing agent and a high grade of tin produced. This is then followed by a complete reduction to produce a slag low in tin so that it could be discarded. The resulting metal is reduced to shot by blowing it with steam in a steam atrosphere. This metal is then chloridized with a gaseous mixture of carbon monoxide and chlorine. The stannous chloride being produced is then electrolyzed by fused salt electrolysis in a cell similar to the Hall cell. The chlorine produced from the cell is fed back into the chlorinator with the carbon monoxide which has been recircled. The tin being molten is tapped from the cell and cast into ingots.

The reactions with the organic chloride gases were not very favorable. They produced a tin organic compound which was free of iron, but they did not react completely with all of the alloy. Aside from this, they would be rather expensive to use on a commercial scale unless they could be produced at a cheaper rate.

VI <u>SUMMARY</u>

The effect of various gases on a solid iron tin alloy, at various temperatures, was studied. From the results of these experiments, those gases which were most promising were studied further. The most promising gases consisted of ethyl, methyl, and vinyl chlorides and phosgene. Phosgene was considered to be superior to the organic chlorides because the reactions would more completely consume the alloy and convert it into the chlorides. Both the organic chlorides and phosgene had the properties of keeping the iron in the residue and volatilizing the tin. Mixtures of carbon monoxide and chlorine could be substituted for phosgene and achieve the some results. Addition of excess carbon monoxide to phosgene, or the mixtures of carbon monoxide and chlorine, had the tendency to hold back the iron while at the same time not appreciably affecting the tin.

Ten grams of alloy, containing approximately 75% tin, the balance iron, had 70.2% of the tin removed without removing any iron. This was accomplished using gas flows for carbon monoxide and chlorine of 126.8 and 31.7 ml./min. respectively, and operating at a temperature of $609^{\circ}C$.

VII RECOMMENDATIONS FOR FURTHER WORK

Further investigation could be carried out with the reactions of phosgene, chlorine, and carbon monoxide. Specifically, the following problems could be investigated:

1. The extent to which pure stannous chloride could be separated from ferrous chloride by volatilization.

2. The exact gas mixture of carbon monoxide and chlorine that would not react with ferrous chloride to produce ferric chloride at various temperatures.

3. Methods of recovering the tin from the stannous chloride produced in these reactions.

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IX VITA

The author was born in Elizabeth, New Jersey on November 26, 1933. He attended Holy Trinity High School for four years and graduated in June of 1951. In September of 1951, the author enrolled in the Missouri School of Mines and Metallurgy and four years later graduated with a Bachelor of Science in Metallurgy.

During the summer between the author's Freshman and Sophomore, and Sophomore and Junior years, he worked in the research Labs of Metal and Thermit Corporation of Rahway, New Jersey. During the summer between the author's Junior and Senior year, he worked for the Research Laboratories of National Lead of Sayreville, New Jersey.

In September of 1955, the author enrolled in graduate school on a cooperative agreement between the School of Mines and the United States Bureau of Mines to pursue studies on the separation of "hardhead" into its const'tuents, iron and tin.

During both the author's undergraduate and graduate studies at the Missouri School of Mines, he has had the job of first, Student Assistant and then Graduate Assistant to Dr. Frad in the Metallurgy Department.