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IMPURITIES IN RECLAIMED LEAD CASTINGS

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IMPURITIES IN RECLAIMED LEAD CASTINGS

I. Introduction

It has been general practice at ORNL to have scrap lead from various sources reclaimed and prepared for re-use by casting into lead brick or other forms of shielding. Some difficulties have arisen from this practice. An investigation has been made to determine the nature of impurities to be found in reclaimed lead and the difficulties which could arise from their inclusion in castings.

II. Multicurie Fission Products Facility Shielded Transfer Carriers

Six carriers weighing approximately 15 tons each were recently poured by the Lead Shop. One of these upon inspection revealed excessive voids or inclusions of lower density material, requiring repair to make the shielding characteristics acceptable. Through conversations with E. E. Pierce, Isotopes Division, and W. S. Hornbaker and O. F. Manuel, Engineering and Mechanical Division, the following information was learned:

1. Used lead was furnished by Isotopes Division for pouring of the carriers.
2. There was not enough of the lead furnished to complete the last carrier. The pouring of this unit was completed by using lead which had been reclaimed and cast into pigs some two to three years earlier for the Isotopes Division. Approximately five tons were used.
3. Upon drilling into some of the "weak" spots in the carrier, a hard, brittle, reddish-brown substance was found to be included. This resembled common red clay which had been fired; and due to

the fact that the design of the carrier did not permit skimming during pouring, it was thought that this might be the trouble. However, this did not prove to be the case.

4. Several tons of the same lead used to complete this carrier remain at the Lead Shop. Many of the pigs exhibit deforming and inclusions. The included material resembles that which was found in the carrier.

III. Specimens Studied

The pigs stored at the Lead Shop were cast in an angle iron mold, making triangular shaped pigs approximately 2 feet long. Many of them exhibit an irregular crater and deformity in the center. Inquiry of the Lead Shop revealed that all sorts of scrap lead had gone into the casting of these pigs for the Isotopes Division. Lead brick, lead melted out of carriers, lead reclaimed from barricades in the isotope shipping area, laboratory sinks, pipe, and a variety of other scrap were melted and recast. These pigs are stored outside, subject to temperature and moisture variations. Deterioration of the pigs was slow, beginning some months after casting and continuing until the present. Some of the pigs still show little or no visible evidence of impurities.

Due to the appearance of the inclusions in the pigs and the F3P carrier, a check was made with T. Tamura, a geologist with the Health Physics Division, concerning the average composition of local red clays. The analysis furnished was:

70% SiO₂
13% Al₂O₃
5% Fe₂O₃
2% K₂O
10% Misc.

Having experienced difficulty with cadmium-lead alloys before, the Lead Shop personnel suspected cadmium as being the source of the present difficulties. Discussions were held with E. E. Hoffman, D. H. Jansen, and C. W. Dollins of the Metallurgy Division concerning this and other possible impurities which could cause trouble.

As a result of these preliminary investigations, four specimens were taken for study. They are as follows:

1. Impurities or inclusions taken from the crater of one of the reclaimed pigs. The material was a hard, brittle, granular, non-crystalline substance. Particle size ranged from $3/8$ " diameter by $1/8$ " thick down to powder. Color ranged from gray to rust, being predominately reddish-brown.
2. Section cut from reclaimed pig. (See Fig. 1)
3. Piece of lead believed to be from barricade in isotopes area. This was some of the lead which went into the reclaimed pigs. The lead was originally installed by a contractor and removed by ORNL forces.
4. Section cut from a lead brick which had expanded, opened up, and spread out. This brick was poured from salvaged lead in the West Burial Ground and was believed to contain cadmium. The original outer surface of the brick showed extreme warpage and fine cracks. Interior surfaces were covered with large crystalline growths. Crystals were dark gray to black with white striations around crystals and on the surface of some of them. (See Fig. 2) This specimen bore no relation to the

current difficulties but was studied as a possible clue to other problems which might arise with reclaiming lead.

Samples were prepared from various areas on all four specimens for Health Physics survey, spectrographic analysis, and chemical analysis. The spectrographic analysis group was requested to look specifically for all those impurities which were known to be possible sources of trouble. These were aluminum, iron and silicon because these were the primary constituents of local clays, and calcium, cadmium, magnesium, antimony, tin and zinc because their presence was either suspected or was known to be a possible source of difficulty in lead alloys. It should be noted that bismuth was not expected to be present in significant quantities.

IV. Results of Tests

In the test results listed below, the number of the sample refers to the specimen number as listed in Section III. The letter designates the area or portion of the specimen from which a particular sample was taken.

HEALTH PHYSICS CHECK

<u>Sample No.</u>	<u>α CPM</u>	<u>β CPM</u>	<u>γ Mr/Hr</u>
	<u>Above Background</u>	<u>Above Background</u>	
1 E	0	0	0
2 G	0	3	0
3 C	0	2	0
4 E	0	3	0

All specimens were found to be well below the recommended tolerance for materials used in the 7000 Area.

RESULTS OF SPECTROGRAPHIC ANALYSIS

<u>Sample No.</u>	<u>Elements</u>											
	<u>Al</u>	<u>Bi</u>	<u>Ca</u>	<u>Cd</u>	<u>Cu</u>	<u>Fe</u>	<u>Mg</u>	<u>Pb</u>	<u>Sb</u>	<u>Si</u>	<u>Sn</u>	<u>Zn</u>
1 C	T	S	M	-	VW	VW	W	VS	M	FT	T	-
1 D	T	S	M	-	VW	VW	W	VS	M	FT	T	-
2 D	T	S	M	-	VW	VW	W	VS	M	FT	T	-
2 E	T	S	M	-	VW	VW	W	VS	M	FT	T	-
2 F	T	S	M	-	VW	VW	W	VS	M	FT	T	-
3 B	T	M	M	-	VW	VW	W	VS	M	FT	T	-
4 C	T	S	M	-	VW	VW	W	VS	M	FT	T	-
4 D	T	S	M	-	VW	VW	W	VS	M	FT	T	-

Explanation of Symbols

VS = Very Strong	VW = Very Weak
S = Strong	T = Trace
M = Moderate	FT = Paint Trace
W = Weak	- = Sought, not found

Since anything which was weaker than a moderate indication on spectrographic analysis would be on the order of a few parts per million and therefore insignificant as an impurity in lead, the chemical analysis group was asked for a quantitative analysis on lead, bismuth, antimony and calcium only.

RESULTS OF CHEMICAL ANALYSIS

<u>Sample No.</u>	<u>Pb (% Wt.)</u>	<u>Bi (% Wt.)</u>	<u>Sb (% Wt.)</u>	<u>Ca (PPM)</u>
1 A	87.8	3.0	0.08	<5
1 B	88.5	3.7	<0.05	6
2 A	87.4	4.4	<0.05	22
2 B	91.9	4.9	<0.05	12
2 C	94.3	4.7	<0.05	9
3 A	99.6	0.09	<0.05	19
4 A	69.3	25.0	<0.2	<5
4 B	74.1	28.5	<0.05	<5

V. Analysis of Test Results

While the data collected are admittedly limited and in some respects inconclusive, certain tentative postulations can be formed. Many binary

and quite a few ternary lead alloys have been extensively studied and reported on in literature. Several lead alloys of four or more constituents are in use in the Babbitts and other bearing alloys, type metals, and various other special applications. However, an analysis of the interactions, properties and behavior of an alloy system composed of all the impurities to be found in the material being considered here would be a difficult and time consuming task.

The fact that aluminum, silicon and iron are present in such minute quantities, and are present even in Specimen No. 3 which is supposedly a commercial grade of lead, indicates that the impurities are not inclusions of red clay. Mr. Dollins indicated that an inclusion of this type should rise quickly to the surface of the melting pot and be removed easily by the skimming process.

Copper, iron, tin and zinc are normally found in all commercial grades of lead; and it is only surprising here that no trace of zinc was found.

In the cases studied, cadmium was not the trouble since no trace of cadmium could be found.

In the case of the lead brick, Specimen No. 4, the high percentage of bismuth present is undoubtedly the cause of the grain growth and expansion.

In the case of the reclaimed pig, Specimen Nos. 1 and 2, the difficulty is probably due to a series of alloys and/or intermetallic compounds being formed with concentrations of certain impurities at the grain boundaries, resulting in an unstable system.

Specimen No. 3, that from the lead barricade, is apparently a low grade commercial lead; and the presence of 0.09 percent bismuth might make its use for general shielding purposes undesirable. This is, of course, based upon analysis of one sample only.

VI. Effect of Impurities on Lead Alloys

The following is a summary of some of the elements which were found as impurities in this lead and some which were not found but are detrimental to the formation of stable lead alloys in general:

Aluminum has a very low solubility in lead. Segregation would occur during cooling of a melt with excess aluminum solidifying first. Lead is used along with bismuth as a minor alloying element in some aluminum alloys to improve machinability.⁽¹⁾

Bismuth and lead have a wide range of solubility.⁽²⁾ They are used in low-melting alloys for fire detection and protection systems, filler for thin-wall tube bending, proof casting and other applications. Bismuth alloys containing 33 to 66 percent lead, even when moderate amounts of other metals are present, usually exhibit growth after solidification and during aging. Some alloys continue to grow at reduced rates for 500 or 1000 hours after casting.⁽³⁾ Bismuth is particularly undesirable as an impurity in shielding lead subjected to neutron bombardment. By successive neutron capture, bismuth is converted to polonium, a strong alpha emitter. The polonium nucleus recoils upon emission of an alpha particle, and it is therefore difficult to contain the contamination.

Calcium forms an unstable alloy with lead. Some phases disintegrate rapidly in moist air. Slowly cooled alloys with 0.03 percent calcium may not show precipitation for a year although disintegration is accelerated at elevated temperatures. (4)

Cadmium is used by the British as an alloying element in lead for cable sheathing. However, there is a slow phase transformation at temperatures below 200° C. which is accompanied by grain growth and grain boundary precipitation which results in eventual destruction of the protective sheath. For this reason, antimony is preferred for use for the same purpose in this country. (5)

Copper as an impurity in lead acts as a hardening agent. It will also form needles of high-melting intermetallic compounds with tin and antimony which give trouble in some casting applications. (6)

It is also an undesirable impurity in reactor shielding.

Iron is not generally considered as a harmful impurity in lead alloys, except that it increases the amount of dross. (6)

Magnesium is added to lead by some manufacturers of bird shot to cause the shot to disintegrate. Even as little as one percent magnesium in lead produces an alloy that is unstable in moist air. (7)

Antimony is used in hardening lead. Alloys containing about one percent antimony are very slow in reaching equilibrium conditions at ordinary atmospheric conditions. The properties and structure may change for many years. (8)

Tin and lead are quite soluble in one another. Tin is not considered a harmful impurity in lead in small amounts except that it may combine with other impurities to form high-melting intermetallic compounds. (6)

Zinc increases the surface tension of lead alloys and at times seriously impairs its ability to be cast, particularly when it is present in amounts greater than 0.1%. (6)

VII. Conclusions

When purchasing lead for shielding purposes at ORNL it has been standard practice to specify commercial chemical lead because of its high purity, particularly its low bismuth content. Other commercial grades have occasionally been purchased for economic reasons, but the purity of such grades has still been in the 99.5 percent plus category.

The samples studied here range from Specimen No. 3 which contains 99.6 percent Pb to Specimen No. 4 which by some accident was alloyed to the extent that it contains only approximately 70 percent Pb. How these impurities came to be included in the reclaimed lead can only be a matter of conjecture since lead from such a variety of sources goes into the reclaiming melts.

Purifying reclaimed lead is a lengthy process requiring the use of special techniques and equipment with which we are not equipped. While it is true that a great many impurities can be removed by the simple melt, agitate and skim process, it is impossible to approach the purity of chemical lead by this process alone as lead alloys very readily with many metallic impurities.

In view of the ease with which impurities could be included in a reclaiming melt due to the tremendous number of lead alloys in use and the number of elemental impurities which could cause difficulties either in castings or in radiation shielding characteristics of the reclaimed lead,

the following recommendations are made:

1. That no lead be reclaimed by the ORNL Lead Shop unless an accurate history of the source of the lead can be provided.
2. That each melt of reclaimed lead be assigned a melt number, that a sample of the liquid melt be taken for quantitative analysis, that a permanent record be made of the melt number and its analysis, and that the melt number be stamped on each item produced from the melt.
3. That the reclaimed lead pigs at the Lead Shop be sold as scrap for re-smelting.

In addition, every effort should be made to control possible sources of cross contamination of melts with metallic impurities, such as the melting of special alloys for customer groups or other abnormal procedures in the Lead Shop.

References

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Fig. 1. Specimen Cut from Reclaimed Lead Pig.

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Fig. 2. Brick Cast from Reclaimed Lead.

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