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Experiments in Treating Zinc-Lead Dusts From Iron Foundries

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Experiments in Treating Zinc-Lead Dusts From Iron Foundries

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EXPERIMENTS IN TREATING ZINC-LEAD DUSTS FROM IRON FOUNDRIES

by

E. G. Valdez[1] and K. C. Dean[2]

ABSTRACT

Iron foundries that melt automobile scrap produce flue dusts averaging about 32 percent zinc and 6 percent lead. Some is sold to smelters, but because of the meager return and difficulty in handling, most of the dust is discarded. As part of the Bureau of Mines program to find uses for mineral wastes, research was initiated to develop an economical process to recover zinc and lead from the flue dust. Research encompassed the extraction of zinc and lead by fuming, leaching, and agglomeration.

Controlled vacuum fuming of zinc to produce Prime Western zinc and a lead-rich residue was the most effective method for treating the dust. This process involved two distillations, or fumings, with carbon and methane as reductants, and resulted in recovery of 91.4 percent of the zinc in a Prime Western grade product, and 98 percent of the lead. Hydrometallurgical techniques involved several leaching methods, but the simultaneous extraction of iron, manganese, and copper resulted in contamination of the solution and made the zinc recovery processes too complicated. Agglomeration was done by pelletizing or briquetting the dust for possible use as feed to a zinc smelter.

INTRODUCTION

Large iron foundries throughout the United States that melt automobile scrap may produce as much as 50 tons per day of flue dust each, for a combined industry total of about 500 tons per day. This dust averages about 32 percent zinc and 6 percent lead. In most cases, the flue dusts have no market value and must be dumped, but containment of the dusts in dumping sites is difficult because the fine particles are readily airborne. Testing was done by the Bureau of Mines, as part of its program on recycling mineral wastes, to find an economic use for the flue dusts and, at the same time, a solution for the disposal problem.

Flue dust samples used in this study were obtained from two west coast producers, each of which accumulates about 50 tons of dust per day. This

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amount is probably insufficient for complete, economical processing at the source. Hence, the possibility of preparing an intermediate product was considered.

In the leaching experiments, zinc and lead were extracted from the dusts with acid or caustic solutions. In the agglomeration research, the dusts were formed into pellets or briquets, using several different bonding agents. A pellet was needed capable of withstanding handling during shipment either to a hypothetical zinc-lead fuming plant at a site accessible to a number of the dust generating foundries, or to an existing, favorably located zinc smelter.

The most feasible approach investigated, however, was double vacuum fuming. Methane was added during the first step to facilitate reduction at a temperature range of 900° to 1,000° C.[3] The experiments were done by selectively reducing the zinc oxide with natural gas under vacuum as proposed by C. G. Maier (3)[4] to produce Prime Western zinc and a lead-rich residue.

DESCRIPTION OF DUSTS

The dusts from both foundries (referred to herein as Dusts A and B) were fluffy, dark brown materials that were difficult to handle and consisted chiefly of zinc, iron, and lead, as shown in table 1. The dusts also contained amounts of less than 1.0 percent of Ag, Au, Bi, Ca, Cd, Cl, Cr, Ga, Mg, Si, Ti, V, and Zr. A screen analysis showed that about 91 percent of the dusts were minus 65 mesh.

TABLE 1. - Partial chemical analysis of flue dusts, weight percent

Dust	Zn	Pb	Fe	Mn	Cu	C
A....	44.5	6.3	21.7	2.6	0.25	0.44
B....	31.5	6.6	22.3	2.4	.3	.45

SPECIFICATIONS OF PRIME WESTERN ZINC

C. H. Mathewson (4) lists six grades of zinc. The lowest commercial grade is Prime Western, used principally for galvanizing steel products. The ASTM Specifications for the various common grades of zinc are given in table 2.

[3]In standard commercial practice, retorts are operated at temperatures between 1,200° and 1,400° C and, as a result, operating and maintenance costs are relatively high.

[4] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

TABLE 2. - ASTM specifications for zinc, weight-percent (1)

	Maximum			Zinc minimum by difference
	Pb	Fe	Cd	
Special high grade......	0.003	0.003	0.003	99.99
High grade.............	.07	.02	.03	99.90
Intermediate...........	.20	.03	.40	99.5
Brass special..........	.6	.03	.50	99.0
Prime Western..........	1.6	.05	.50	98.0

LEACHING

Leaching methods were tested to extract zinc and lead in two steps. To extract zinc as sulfate, the procedures tested were (1) sulfuric acid leach, (2) sulfuric acid bake and water leach, and (3) ferrous sulfate bake and water leach. Caustic leaching and hot acid brine leaching were tested to extract lead from the residues resulting from the leaching of zinc. Iron oxide was expected to be concentrated in the final residue.

Sulfuric Acid Leach

Selective leaching of zinc from dust was tested at several levels of pH by the gradual addition of H_2SO_4. The tests showed that 70 percent of the available zince was selectively leached at a pH of 4.0. Higher zinc recoveries were attained at lower pH values, but iron was also extracted.

Sulfuric Acid Bake and Leach

A variation of acid leaching was to pug or to wet the dust with 50 percent acid, then bake at 650° C with the objective of forming water-soluble zinc sulfate while oxidizing iron to an insoluble form. A subsequent water leach dissolved 90 percent of the zinc, but the solution was contaminated with iron, copper, and manganese.

Ferrous Sulfate Bake and Leach

Ferrous sulfate was tested as a sulfating agent. Pickle liquor, a waste product from steelmaking, was used as the source of ferrous sulfate. The dust was pugged with enough liquor to supply an excess amount of ferrous sulfate, then baked at 650° C and water leached. Seventy-five percent of the zinc was extracted, but again the solution was contaminated with iron, copper, and manganese.

Caustic Leach

Zinc can be extracted from oxidized ores by a strong NaOH solution, which can be electrolyzed to produce metallic zinc (2). To determine if zinc and lead in the flue dust could be extracted, dust samples were agitation-leached for 2 hours at 70° C in solutions containing 700 grams per liter of NaOH. Maximum recoveries were 43.7 percent of the zinc and 82.3 percent of the lead.

Dissolution of Lead in Hot Acid Brine

Except for the caustic-leached residues, all of the other residues recovered from the preceding leach tests were treated with a saturated NaCl brine that was acidified to a pH of 3.0 with HCl to extract lead as a chloride complex. Lead extractions averaged only about 50 percent. A pure $PbCl_2$ product was produced by cooling the pregnant brine solution.

AGGLOMERATION

Another approach considered for utilizing the dust was the agglomeration of the dust into briquets or pellets suitable for use as feed to zinc smelters.

Two agglomerating techniques were investigated using a blend of 95-percent flue dust and a 5-percent carbon mixture dust, and a bonding additive. The bonding additives tested were calcium lignosulfonate, hydrated lime, a bituminous-coal product diluted with kerosine, fire clay, borax, bentonite, and a resinous adhesive in amounts of 1 to 2 weight-percent. The first method involved adding water to the blend, and briquetting at 2,000 and 5,000 psig with a hydraulic press. The second method involved pelletizing the blend in a rotating drum while spraying with water.

To determine the strength or stability of the pellets and briquets, an empirical shatter test was employed in which a 250-gram sample of each of the products was placed in a plastic sack and dropped six times on a concrete floor from a height of 70 inches. The shattered products were screened through a 6-mesh screen to determine the weights of the oversize and undersize fractions to calculate a stability factor. The stability factor, a measure of green strength and expressed in percent, was determined by dividing the total weight of the sample before shattering into the weight of the plus 6-mesh fraction after shattering. The stability factor of the pellets prepared with 1-percent bentonite was 90.2 percent, which was only slightly less than the maximum of 93.9 percent attained with Coherex.

Qualitative observations and shatter data indicated that pellets formed with 1-percent bentonite and 6.5-percent water in a rotating drum would be the least costly, easiest to prepare, and appeared strong enough to withstand handling during shipment.

VACUUM FUMING

The objective of testing the fuming method was to produce Prime Western zinc and a lead-rich residue salable to lead smelters. This technique is a modified form of a procedure developed by Maier (3), who used methane to reduce pure zinc oxide at temperatures near 1,000° C. Modifications encompassed the use of two fuming steps instead of one, and the combined use of methane and carbon as reductants instead of methane alone. The use of methane or natural gas allowed the fuming to be carried out at temperatures ranging from 900° to 1,000° C, as opposed to the temperature range of 1,200° to 1,400° C required when carbon alone is used. It was expected that a zinc-lead product would be fumed off in the initial step, and the Prime Western zinc and the lead-rich residue would be produced by refuming the composite.

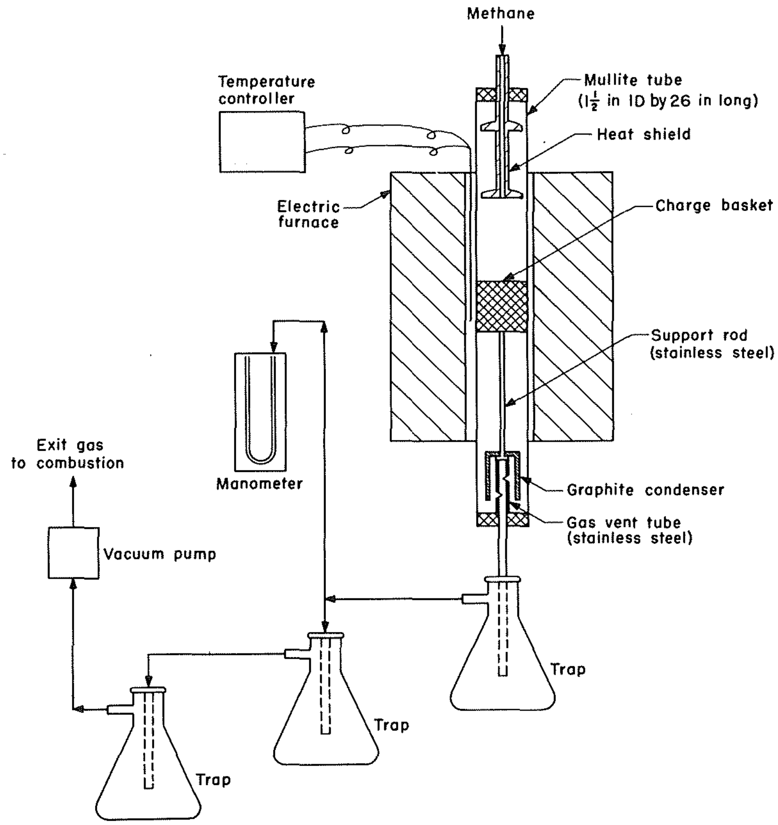

FIGURE 1. - Primary fuming apparatus.

Equipment and Procedure

The reactor, furnace, and accessories used for the fuming tests are shown schematically in figure 1. Methane gas was metered through a flowrator, entered the top of the reactor, and flowed past a ceramic radiation heat shield into the hot zone of the furnace. At this point, the gas reacted at 950° C under a vacuum of 24.5±0.5 inches of mercury with a 60-gram pelletized charge contained in a stainless steel wire basket. Fumed products flowed downward and were deposited on the supporting stainless steel rods and on an inverted graphite crucible.

Traps located between the furnace and the pump collected small amounts of the carried-over product. At the end of the run and after cooling, the furnace was emptied, and the condensed product and trapped dust were combined and refumed to separate zinc from lead in the apparatus shown in figure 2. Refuming was done at 650° C under a vacuum of 22 to 25 inches of mercury, and zinc was deposited on a solid graphite condenser located at the bottom of the furnace. A lead-rich residue remained in the crucible.

Test Variables

A series of fuming tests with dust A was carried out to determine the best overall conditions of temperature, retention time, feed particle size, vacuum, and methane and carbon requirements to achieve maximum zinc and lead recoveries. Results of the tests to determine these parameters are described in the following paragraphs. Unless otherwise specified, tests conducted to study the effects of temperature, retention time, vacuum, and volume of methane were carried out with pellets containing 5 percent carbon.

Results

Feed materials with and without bonding additives, and ranging in size from minus 6-mesh pellets to 1-inch-diameter hydraulically pressed briquets, were tried in the primary fuming furnace. The comparative tests revealed that

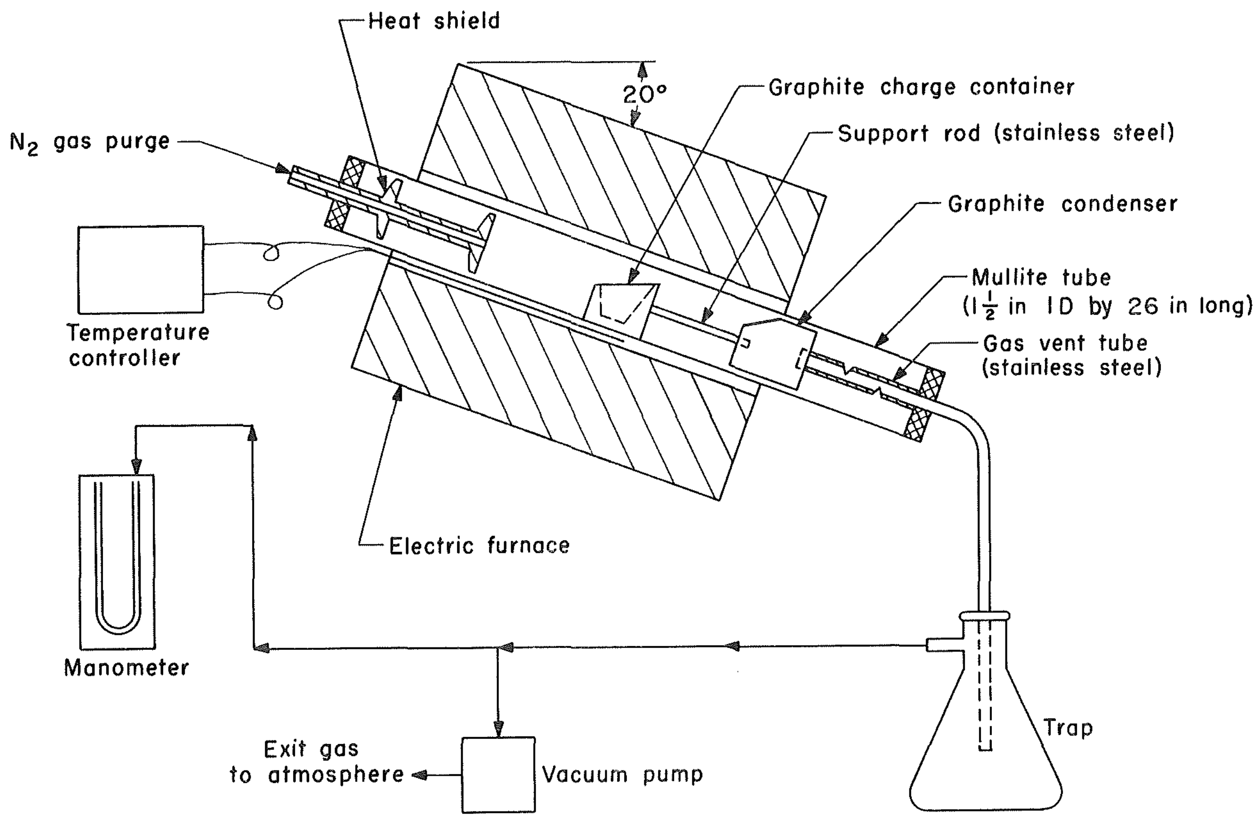

FIGURE 2. - Secondary fuming apparatus.

minus 3/8-inch plus 6-mesh pellets prepared with coke and water in a rotating drum were sufficiently stable to withstand rough handling and were most suitable for use in the primary fuming furnace. These pellets were prepared for vacuum fuming by blending the minus 35-mesh foundry dust with 5-percent minus 65-mesh petroleum coke and agglomerating the mix with 16 percent water in a rotating drum. The plus 3/8-inch fraction was crushed, combined with the minus 6-mesh fraction, and repelletized. Pellets were dried in ovens at 100° C, sampled, and analyzed. A partial chemical analysis of the pellets was, in weight-percent, 30.6 zinc, 6.3 lead, 20. 6 iron, 5.2 carbon, 2.2 manganese, and 0.77 sulfur. Owing to their compactness, the hydraulically pressed briquets inhibited the fuming of zinc and lead.

To study the effects of carbon, pellets containing from 0 to 13 percent carbon were processed in a vacuum at 950° C in the presence of methane. Results showed that in the absence of carbon, only 64 percent of the zinc was volatilized; with about 5 percent carbon, 99 percent of the zinc fumed off. The effect on lead was less significant; recoveries were 96 percent without carbon and 99 percent with carbon. Addition of carbon in amounts greater than 5 percent did not improve recoveries. On the other hand, the volume of methane present in the system greatly influenced the amount of lead fumed off. For example, 8,350 cubic feet of methane per ton of pellets fumed off 10 percent of the lead and 99 percent of the zinc, whereas 13,370 cubic feet fumed off at least 98 percent of each. Exit gas composition at the high flow rate, in volume-percent, was 4.7 for CO_2, 39.3 for CH_4, 19.1 for CO, and 37.2 for H_2.

Recoveries also varied with the amount of vacuum imposed on the system during the primary fuming. At zero vacuum, the recoveries of zinc and lead were 81 percent and 6 percent, respectively; with a vacuum of 10 inches of mercury, the recoveries were 95 percent of the zinc and 5 percent of the lead. Boosting the vacuum to 25 inches increased the recovery of each to 98 percent. Tests at temperatures ranging between 750° and 1,000° C revealed that maximum recoveries were attained at 950° C. It was established that 90 minutes in the primary furnace was sufficient time to fume off 98 percent of the zinc and lead in the pellets.

The zinc-lead condensate from the primary fuming was scraped from the graphite condenser and charged to a graphite boat for secondary fuming. An overall summary of the conditions best suited for fuming zinc and lead in the primary furnace, and zinc in the secondary furnaces, are given in table 3. The chemical composition of the recovered products is presented in table 4. The zinc product, in addition to the elements shown, contained 0.06 percent cadmium and 0.05 percent oxygen.

TABLE 3. - Conditions for maximum recoveries

Parameters	Primary fuming	Secondary fuming
Retention time....................................minutes..	90	120
Temperature...° C..	950	650
Carbon requirements.....................weight-percent..	5	0
Vacuum requirements..................inches of mercury..	24.5±0.5	22-25
Methane requirements......cubic feet per ton of pellets..	13,370	0
Zinc recovery....................................percent..	98	93
Lead recovery.......................................do.....	98	<1

TABLE 4. - Chemical composition of products, weight-percent

Components	Zn	Pb	Fe	C	Mn	S
Primary furnace residue...	<0.1	0.1	51	0.2	5.5	-
Zinc-lead composite.......	71	10	.1	.1	.002	-
Secondary furnace residue..	12	50	.4	-	-	0.6
Zinc product.............	[1]99	.8	.01	-	<.001	<.01

[1]Determined by difference.

Treatment by double vacuum fuming produced two products--a fumed fraction that contained 91 percent of the zinc as Prime Western zinc, and a furnace residue that contained 97 percent of the lead as a 50-percent lead product. Results for dusts A and B were about the same.

PROPOSED FUMING PLANTS

Materials and equipment flowsheets for the proposed fuming plants are shown in figures 3-4. Figure 3 outlines the two-step vacuum process; figure 4 outlines the conceptual one-step process. Through the 950° C fuming retorts, the flowsheets are identical. The primary fuming retort is a 12-inch-ID, 15-foot-tall stainless steel shell lined with graphite, which operates at a vacuum of 24.5±0.5 inches of mercury.

In the two-step process, vapors pass through primary condensers where the fumed products are collected as molten metals. The molten melt is fed to secondary retorts, where the temperature is maintained at 650° C under a vacuum of 24.5±0.5 inches of mercury. Lead containing a small amount of zinc is retained in these retorts as molten metal, and the zinc is vaporized and drawn through secondary condensers where zinc of Prime Western grade is collected. The gaseous byproduct drawn from the primary vacuum furnace through the primary condensers contains substantial amounts of carbon monoxide and hydrogen. This gas passes through a water-cooled heat exchanger ahead of the vacuum pump, is mixed with makeup methane, and is used as fuel to heat the primary retort furnaces.

In the conceptual one-step vacuum process, the secondary retorts are eliminated and the separation of lead and zinc is done by fractional condensation in two separate condensers. Vapors from the retorts pass through the primary condenser where lead, containing a small amount of zinc, is collected as molten metal, and the zinc vapors flow through to a second condenser where Prime Western grade zinc is collected. Similarly, the gaseous byproduct from the retorts contains carbon monoxide, which is enriched with methane and used as fuel to heat the retort furnace.

The preliminary cost estimates were based on treating 47.5 tons per day of flue dust to produce 6.1 tons of lead-zinc alloy, 20 tons of iron oxide-rich residue, and 13.3 tons per day of Prime Western grade zinc. A 24-hour day and a 7-day week (350 days per year) were used for the evaluation. Equipment costs were adjusted for the second quarter of 1973 (M&S Index 344), and a linear depreciation over a 12.5-year life was assumed. A labor rate of $4.45 per hour was chosen for the operation. Price for coke was estimated at $32 per ton, and flue-dust costs of $0 and $10 per ton were assumed. At a rate of return on investment of 35 percent calculated on a cash flow basis, the respective zinc production costs were $0.21 and $0.23 per pound for the two-step fuming process, and $0.19 and $0.21 per pound for the one-step conceptual fuming process. Estimated annual operating costs and 1973 capital costs for the two-step vacuum fuming plant are presented in tables 5 and 6, respectively. These costs are not much higher than those of the conceptual plant with annual operating costs and 1973 capital costs of $971,000 and $2,951,000, respectively.

TABLE 5. - Estimated annual operating costs for foundry flue dust treatment plant

DIRECT COSTS	
Materials and utilities:	
Foundry flue dust (16,625 tons)	$0
Coke (875 tons × $32/ton)	28,000
Electricity (3,274.7 MkW-hr × $0.01/kW-hr)	32,700
Natural gas (48,805 Mcf × $0.0005 cf)	24,400
Total materials and utilities	85,100
Direct labor:	
Labor $4.45/man-hour	194,400
Supervision (15 pct × $194,400)	29,200
Total direct labor and supervision	223,600
Maintenance:	
Labor	68,500
Supervision (20 pct × $68,500)	13,700
Materials	68,500
Total maintenance	150,700
Payroll overhead (25 pct × $306,000)	76,500
Operating Supplies (20 pct × $150,700)	30,100
Total direct costs	566,000
INDIRECT COSTS	
Administration and overhead (40 pct × $404,400)	$161,800
Fixed costs:	
Taxes and insurance (20 pct)	55,300
Depreciation (12.5 years)	290,200
Total annual operating cost	1,018,000

TABLE 6. - Estimated 1973 capital costs for foundry flue dust treatment plant

Fixed capital for fuming plant	$2,406,400
Facilities (10 pct × $2,406,400)	240,600
Utilities (12 pct × $2,406,400)	289,000
Total fixed capital cost	2,936,000
Working capital	237,000
Total capital	3,173,000

Although the economics of the processes appear favorable, it should be emphasized that the design of the retort furnaces and the condensers are not based on actual pilot plant operating data, but rather on laboratory work done in a 2-inch-diameter furnace. The residence time of 9 hours for the pellets in the furnace is calculated on a comparison of furnace diameters. The accuracy of these assumptions is questionable; consequently, the cost estimate is useful only as a basis for considering future larger scale experimentation.

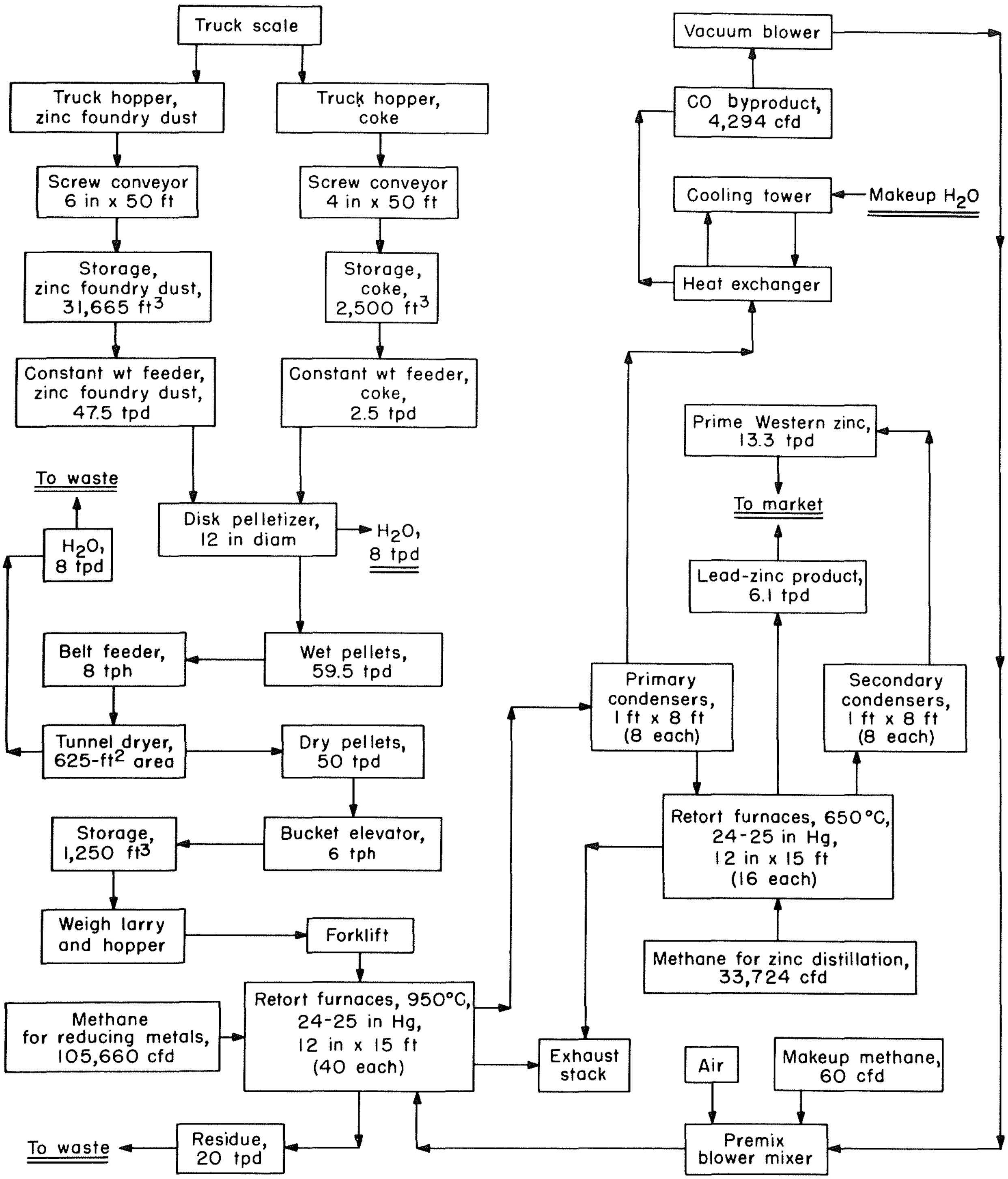

FIGURE 3. - Flowsheet of two-step vacuum fuming plant for recovering zinc and lead from foundry flue dust.

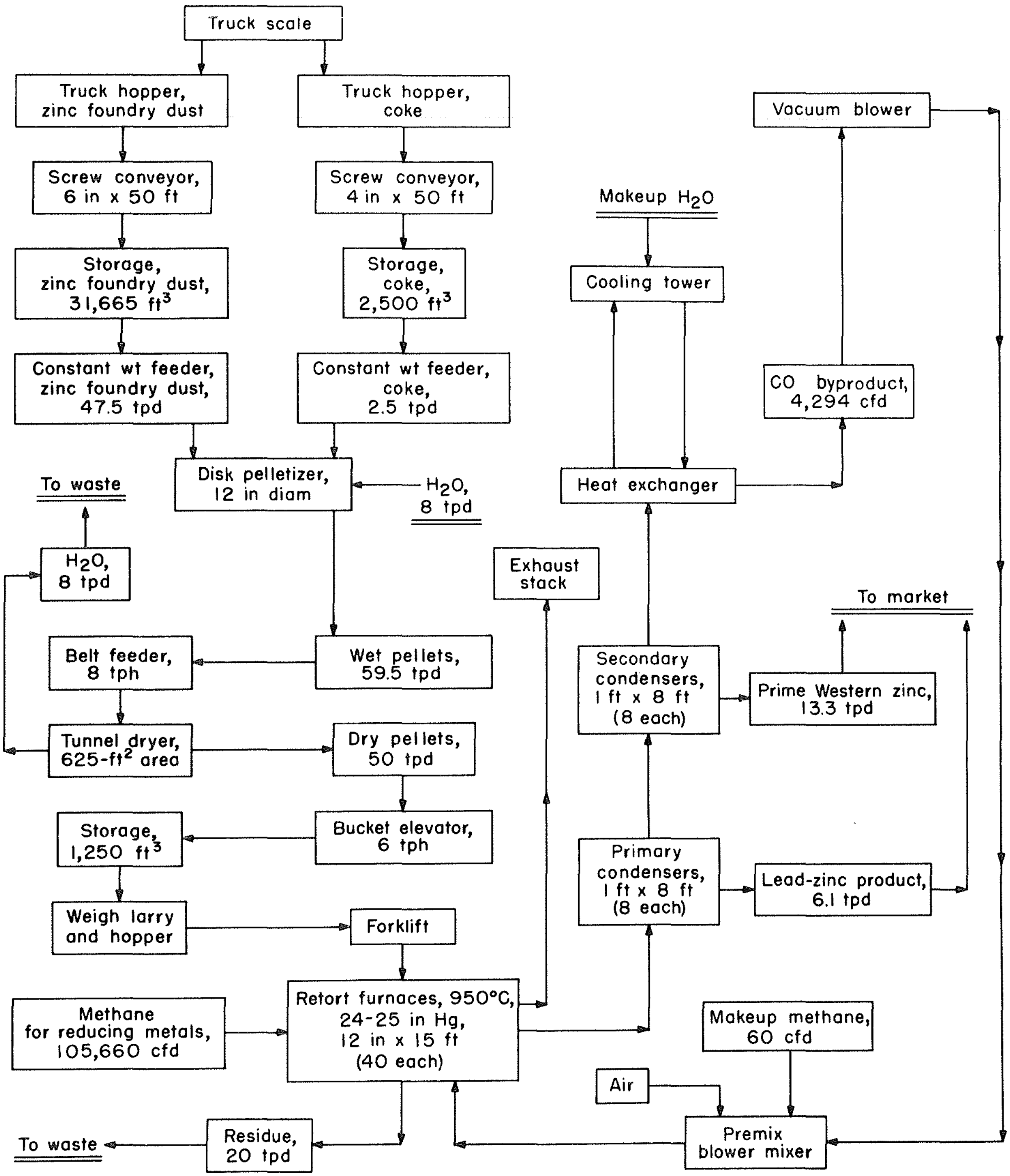

FIGURE 4. - Flowsheet of conceptual one-step vacuum fuming plant for recovering zinc and lead from foundry flue dust.

CONCLUSIONS

If foundry flue dusts could be sold directly to zinc smelters, pelletization before direct shipment would probably be the preferred method for disposing of the dusts.

Leaching and fuming were examined as means by which the zinc and lead could be recovered at the smelter. Leaching is not considered feasible because other minerals are extracted simultaneously with the zinc and lead. Fuming appears to be the most practical method for zinc and lead recovery. Preliminary estimates for a two-step and a conceptual one-step process indicate that fuming may be economically practical, but further research is recommended.

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