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UNIVERSITY OF ALBERTA

HYDROMETALLURGICAL BATTERY RECYCLING: A PILOT PLANT STUDY

by

WILLIAM MOURE JR.

A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled HYDROMETALLURGICAL BATTERY RECYCLING: A PILOT PLANT STUDY submitted by WILLIAM MOURE JR. in partial fulfilment of the requirements for the degree of MASTER OF SCIENCE in METALLURGICAL ENGINEERING.

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Date. July 17, 1989 ....

Abstract

Environmental laws enacted in the 1970's and 1980's have had a major impact on the lead recycling industry. Many battery processors and smelters have been shut down by the tightened restrictions on worker exposure to lead and on lead and sulphur emmissions to the environment. However, this has yet to spark the implementation of "cleaner" hydrometallurgical technology on an industrial scale.

In this study, a bench scale pilot plant was designed and built to investigate the effectiveness of ammoniacal ammonium sulphate leaching (the AAS Process) for battery recycling. The major pilot plant equipment consisted of a leaching column, settling tank and electrowinning tank. The leaching column effected a physical separation of the metallic lead pieces contained in the (crushed battery material) feed, while dissolving the lead compounds. The settling tank was necessary to clarify the AAS [illegible] removing the insoluble PbO_2 and undissolved $PbSO_4$ and PbO. Finally, the dissolved lead was recovered by electrowinning.

The only inputs to the process were NH_3 (to make up for evaporation and $(NH_4)_2SO_4$ production) and electricity for electrowinning. All products produced by the process were useful: hard lead from the metallics in the feed, soft lead from electrowinning and $(NH_4)_2SO_4$ which is saleable as fertilizer.

Optimization of the plant operating variables revealed the strong interdependence of the operating parameters and

the tradeoffs which occur between the various operating efficiencies. Recoveries of lead from the lead compounds in the feed (without recycling the settling tank slimes) were generally around 60% (with electrowinning current efficiencies as high as 80%). Any undissolved lead compounds could be treated with H_2SO_4 (to convert the insoluble PbO_2 to soluble $PbSO_4$) and returned to the leaching circuit to effect a virtual 100% recovery rate.

The pilot plant successfully demonstrated the suitability of the AAS process for recycling lead-acid batteries. The process uses reasonably inexpensive inputs, produces no undesirable byproducts and, most importantly, solves the environmental problems which plague the pyrometallurgical methods currently employed by battery recyclers.

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I. INTRODUCTION

"Recycling of lead scrap is an economic necessity since lead mining and production is only able to cover a maximum of three quarters of worldwide demand. Lead is furthermore one of the most important metals for recycling due to its toxicity..." [1]

In fact, in 1983/84, recycled lead constituted approximately 38% of total world refined lead production. In Canada, it was 28% (71,000 tonnes) and in the United States it was more than 50% (488,000 tonnes). The end uses for lead show just how important lead-acid batteries are in the lead industry. In the United States in 1984, storage batteries accounted for 72% of lead consumption; metal products accounted for 8%, chemicals (including petroleum) for 13% and all other uses for 7%.[2] The lead used in petroleum and pigments is not recyclable and metal products have a relatively long service life. Therefore, storage batteries with their average life of 2 to 3 years constitute the most important source of recyclable lead.

With the large source of adaptable technology available from the primary lead industry and the experience gained over many years of recycling batteries, secondary lead smelting has become a very efficient and competitive industry. However, much of the increased activity of environmental regulatory agencies has focussed on the lead industry and battery recyclers in particular.

In the United States, in the late 1970's, there were over 300 independent companies processing batteries for secondary lead smelters; in 1985 only 4 were still operating. Of the 22 secondary lead smelters active in 1985, it has been predicted only 9 will still be in operation in 1990.[3] The reason for these business closures is that the industry was hit hard by two sets of regulations. The first, enacted in the late 1970's, was the Occupational Safety and Health Administration's (OSHA) regulations which cut the lead-in-air limit in the workplace from 150 micrograms per cubic meter of air to 50 micrograms per cubic meter. The second was the Environmental Protection Agency's (EPA) classification of scrap batteries as hazardous waste. For companies handling batteries, this has consequences in the storage and transportation of batteries and for the disposal of any byproducts from processing. Special licencing and insurance regulations must also be complied with.

As a result of the EPA's activity in the secondary lead industry, in 1985 approximately 20% (120 companies) of the EPA's list of hazardous sites slated for cleanup were sites abandoned by companies involved in lead recycling. One example of such a cleanup involved the excavation of all contaminated soil and sediments with disposal into a facility constructed to Class I Sanitary Landfill Standards, treatment and discharge of all surface water, groundwater removal and treatment of the underlying aquifers as well as monitoring of all potable water wells within a one mile radius of the site.[4] Such extensive cleanups are obviously expensive.

What this has done is set the stage for the introduction of new technology. Such technology, however, has not yet been forthcoming on a commercial scale. Lead smelters can now attribute up to 44% of their capital costs and up to 62% of their energy requirements to pollution control facilities.[5] This only reduces the problem, however, it does not eliminate it. Such smelters must be operated on a relatively large scale to gain the advantage of economies of scale. Then, the problems involved in the collection and transportation of enough batteries to feed the plant must be dealt with.

What this study attempted to do was, by means of a literature survey, determine what processes are available or have been studied that could be applied to battery recycling. The most promising of these was then further developed through to the construction and testing of a small scale pilot plant.

II. LITERATURE SURVEY

In an effort to determine the best approach to battery recycling, one must be aware of the alternatives available. This includes both the industrially employed methods as well as processes currently being researched. The objectives of this literature survey were to determine the methods by which batteries are currently being recycled, outline the advantages and disadvantages of each process and see how current research is attempting to solve the problems whether through improvements to the methods in use or developing new methods. Finally by looking at all the data, one may try to determine what method or combination of methods shows the most promise.

In order to understand what is required in processing storage batteries, one must first understand the nature and purpose of the battery's components. A battery consists of a hard rubber or polypropylene outer case, which holds the other components intact and provides a reservoir for the acid. Inside are positive and negative grids, separated by fibrous or PVC separators. The grids are made of a 6 to 12% antimonial lead alloy and are connected by bars made of the same alloy.[6] The connecting bars have posts which exit the case and allow the battery to be connected to an outside circuit.

The positive grids are covered with a PbO_2 paste and the negative grids with spongy lead, all immersed in a sulphuric acid electrolyte. Electrical power is obtained from the cell by the conversion of lead and lead dioxide to lead sulphate.

$$Pb + PbO_2 + 2H_2SO_4 = 2PbSO_4 + 2H_2O \qquad (1)$$

The potential of this reaction is approximately two volts, so a battery consists of a number of cells connected in series to obtain the desired voltage.

When a battery is spent, the components degrade by various means (short circuiting, sulphating of positive grids, etc.), so that the battery can no longer be fully recharged (i.e., the reverse of equation 1). In this condition, the paste fraction of the battery consists mostly of $PbSO_4$ with variable amounts of PbO_2 and PbO. Thus, when scrapping batteries it is possible to separate five fractions. These are the electrolyte, the case material, the separator material, the metallics (grids, bars and posts), and the lead compounds called the active material or pastes.

Approximately 85% [7] of all storage batteries are the standard automotive type or SLI battery (starting, lighting and ignition). Once drained of acid, the lead and lead products constitute approximately 75% to 90% of the battery's weight; an average of 10 kg contained lead per battery.

The methods which can be used to process spent batteries can be classified into three general catagories. Mechanical processing involves breaking the batteries and classifying the material into the separate battery components (i.e., metallics, case and separator material, and the battery pastes). Secondly, pyrometallurgical processing is used to melt the metallics and/or reduce the pastes to metallic lead. Thirdly, hydrometallurgical processing can be used to treat the pastes to obtain pure lead, pure lead compounds or a product more amenable to pyrometallurgical processing. Any recycling scheme can involve unit processes which fall into any or all of these general categories.

A. MECHANICAL PROCESSING

The objective in processing batteries mechanically is to separate the lead containing material, the acid, the plastics and the separator material. In order to derive maximum economic benefit from this processing it is usually desirable to also separate the pastes from the metallics. This enables subsequent processing to produce an antimony rich lead alloy from the metallics and pure lead from the pastes. If metallics and pastes are processed together, the result is a lead alloy of intermediate antimony content. Other desirable features include avoidance of manual work (exposure of workers to acid), high recoveries, and low capital, operating and maintenance costs.

Before the advent of the modern battery breaking plants, batteries were broken manually using axes, saws or guillotines. The plastics were removed by hand and the metallic lead and pastes were melted on the spot or shipped to (primary) lead smelters. Even today, manual breaking is by no means extinct.

For modern operations, two methods of comminuting batteries are popular. In smaller plants, the tops are sawn off the batteries, enabling the contents to be dumped out by hand. The tops are then put through a hammermill to liberate the posts from the plastic. Larger plants favour a shearing mill which uses rollers equipped with disc-shaped cutting blades. The shearing action is more effective on the polypropylene cases which are now much more common than hard rubber cases.

Classification of the various components is most often accomplished using differences in size or specific gravity. In breaking batteries, the paste is for the most part knocked off the grids and reports to the "fines". The metallics and plastics are reduced according to the size of the crusher or shear, thus constituting a larger size fraction. To utilize this difference, screens are most commonly used. The components can also be separated by their specific gravity. Metallics have a specific gravity of 9-10, the active material 4 and the plastics and separators 1.4-1.8.[8] Various methods are employed to take advantage of this difference including sink/float or heavy media separation, hydrocyclones, spiral classifiers, elutriation, etc. Breaking plants use these and other methods, in various combinations, to achieve their specific objectives.

Commercial Operations

In the operations using heavy media, the two popular media are the lead fines produced by the operation itself and magnetite. The lead fines are inexpensive and readily available, whereas magnetite has the advantage of being easily recovered by magnetic separation (battery fines must be recovered by solid/liquid separation).

The *Tonolli Process* is a patented mechanical process popular with many battery processors. Batteries are broken in a large rotating drum. The drum is fired with a gas burner which vaporizes the acid and dries the components. With internal augers, fines are removed from one end and fragments from the other. A sink/float process is then used to separate the plastics and metallics in the "fragment" fraction.[9-11]

The *BBU Process* (developed and used by **Bleiberger Bergwerks Union**) involves crushing batteries with a rotary shear and subsequently drying in a rotary drier. The drier helps ensure the grid material is completely disintegrated. With a vibrating screen, fines are removed, then separators are pneumatically drawn off (and separated with a cyclone). The battery paste is mixed with dust from the various air filtering systems and moistened to a "dust-free" state. Small pieces of grid material are removed from the fines by milling and separating in a zig zag sifter. The remaining fines (consisting mostly of paste material) can then produce soft lead with a minimum of refining. The coarse fraction from the screen is conveyed through a "combined washing drum". The first compartment is filled with a heavy medium (water - lead sludge mixture, density of 1.8 g/cc) which separates the plastics from the metallics and the second compartment washes these two fractions. The wash water is recycled via a thickener. The recycled water is used in moistening the fines and the lead sludge is collected and treated (both are used for maintaining the heavy medium).[9, 12]

At **Stolberger Zinc A.G.**, the mechanical processing produces three materials: metal, "middlings" and a slurry. The grid metal is simply melted, the slurry is sintered for blast furnace feed and the middlings are fed to the blast furnace with the sinter. The function of their breaking plant, then, is to remove the plastics, separators and acid and to separate out the large metallic pieces which do not need blast furnace treatment. To process, the batteries are crushed with a roll crusher and the separators are removed with a 60-80 mm mesh sieve. A 5 mm screen is used to separate fines which are further treated in a spiral classifier to yield a slurry and middlings. The coarse fraction from the 5 mm screen is treated in a magnetite heavy medium to float off the casing fragments.[13, 14] Changes have recently been made to this process due to the increasing proportion of polypropylene cased batteries (the polypropylene does not break up as easily as the hard rubber casings). Shredding is now done in a single stage with counter-rotating crushing rolls, furnished with disc shaped cutters. Another change is the use of a hydrocyclone to separate lead bearing material from the plastics.

Batteries are transported to **N.L. Industries Inc.**'s Pedricktown decasing plant by tractor trailer. The batteries are unloaded "en masse" by a truck dumper which lifts the tractor trailer to 60° from the horizontal. The batteries are then fed into a shredder (again with disc shaped cutting blades) with a payloader. After shredding, the first stage of separation is a trommel which splits the product into +0.8 and -0.8 cm fractions (the shredder product is nominally -5 cm). The +0.8 cm fraction is treated in a magnetite heavy medium to float plastics and separators away from the grid metal. The -0.8 cm fraction is treated with a spiral classifier and screen to give a paste and a middlings fraction. The lead materials are dewatered and dried prior to smelting and battery casings are sold to a plastics manufacturer.[15]

Penarroya's battery wrecking consists of a crusher followed by screening. The fines go directly to smelting while plastics and separators are removed from the coarse fraction in hydraulic separators (using upward flowing water). The metallics from the coarse fraction are melted separately.[5]

As with **N.L. Industries**, **RSR Corporation** uses a truck dumper for unloading batteries at their Dallas plant. The wrecking operation is a modified *Tonolli Process*. Crushing is done with double or single roll impact crushers or with knife shredders. After crushing, a heavy media separator is used to float off plastics and separators; the battery fines are used for the heavy medium. The float from the heavy media separation goes to a water only sink/float system to separate the polypropylene from the hard rubber and separator fragments. The polypropylene is sold to plastic recyclers and the rubber is used as a source of carbon reductant in the smelting operations. The fines forming the heavy medium are recovered in a clarifier and all the lead-bearing material is treated together in subsequent pyro-processing. The dilute acid and washwater are neutralized, filtered and disposed of into the sanitary sewer system.[16]

Although many more battery breaking operations are in existence, the above are the ones best detailed in the available literature. In addition, many patents have been taken out for mechanical processing methods which are in use industrially (whether under licence or not). These processes include comminution with screening,[17-19] sink/float systems using water[20] or heavy media,[21-24] spiral classification, air classification,[25 26] sintering for blast furnace feed,[27] or combinations of the above.[14 28-37]

Research

A study by **Chumachenko, et. al.** compared the separation efficiency of heavy media separation, a shaking table, spiral concentrator, jet classifier and wet cyclone. Best results were found using 2 stage crushing (jaw crusher then knife type shredder), screening, then classification with the cyclone using heavy media. The heavy medium was made from a slurry of the battery paste material.[8] Others have patented or studied various separation processes utilizing the hydrocyclone.[38-40]

Trommels have been investigated for use in various ways. In one patent, batteries are ground in a drum charged with grinding balls, forming a heavy medium to float organics for removal. Two trommels are then used to separate the metallics and wash them. The suspension is then pumped back to the grind drum and part is withdrawn through a thickener for fines removal.[41] Another process described is much the same except the drum is not used for grinding, only for forming the heavy medium; the metallics, slurry and nonmetallics are all separated in the same drum.[42] In another case, only one end of the drum is a screen and several internal augers move the metallics and nonmetallics [illegible] the ends of the drum. The metallics are separated from the waste material slurry by the screen.[43]

Instead of heavy media, some investigators have tried using a column with upward flowing water. The flow rate is such that metallics sink, plastics are entrained and washed out of the column (and screened) and the paste forms a slurry and is recovered by settling.[44,45]

One novel technique uses the specific gravity of the components to sort them. The battery material is ground fine (<3 mm) and the slurry is fed onto a rotating cone. Particles adhere to the cone by the surface tension of the water and are thrown off at different levels along the cone by centrifugal force.[46]

B. PYROMETALLURGY

In order to obtain a product saleable to lead consumers, the component materials recovered from batteries must be converted into metallic form. In general, this means casting the metallic scrap into ingots (to eliminate water, plastics and dross) and by some means reducing the lead compounds into metallic form. The reduction of lead compounds can be performed in a variety of ways; industrially it is performed almost exclusively by pyrometallurgical operations. Two schools of thought exist in this area: those that feel it is more profitable to mechanically separate the battery components enabling the production of both soft and hard lead and those who believe the direct smelting of whole batteries, producing only hard lead, is economically justified by the savings accomplished in the elimination of mechanical processing.[47]

Pyrometallurgical reduction can be carried out in a variety of furnaces. Probably the largest tonnage of secondary lead is still produced in blast furnaces, but rotary furnaces are becoming very popular in smaller operations. Other operations use reverberatory, electric, induction, or crucible furnaces.

The "conventional" smelting operation involves smelting scrapped batteries, or components thereof, with soda ash/limestone/scrap iron fluxes and coke or coal added as a fuel and reducing agent (fluxing practice varies between individual operations). The lead oxides and lead sulphate are reduced to metallic lead, with the coproduction of carbon monoxide, carbon dioxide and sulphur dioxide. For pollution control, the offgases are treated in an after-burner, then cooled and filtered. Most operations have some provision for slag cleaning (to remove entrained lead) either in the same furnace used for reduction or in another facility.

Industrial Processes - Direct Smelting

In direct smelting of batteries, whole drained batteries are smelted in order to eliminate the mechanical processing step and to use the case as part of the fuel requirements for the process.

In the *Varta Process*, whole drained batteries are fed directly into a shaft furnace with fluxes, a reducing agent and other concentrates.[9] It has been reported that this method has been operating reliably for some processors for over 10 years.[48]

In the *Oliforno Process*, the batteries are melted by themselves in a rotary kiln. The lead-slag mixture is granulated and then smelted with fluxes in the rotary kiln.[9]

The **Britannia Lead Company** (England), also employs direct smelting with its blast furnace. Some batteries are fragmented and some are fed whole (whole batteries constitute 30-40% of the charge). The charge also contains softening skims, lead residues, foul slag from their rotary furnace and dry and caustic refining skims. Fluxes used are chalk, iron, metallurgical coke and return slag. Offgases are afterburnt and then filtered in a baghouse. The baghouse dust is agglomerated and recycled. Other equipment used by Britannia are a lead kettle floor for softening lead, a moulding machine and a rotary furnace.[49, 50]

The operations of **Paul Bergsoe & Son** also use a blast furnace for the direct smelting of large quantities of whole batteries. The batteries are pierced to drain the acid, then coke, iron oxide, iron, limestone, scrap lead, furnace slag and agglomerated flue dust are all fed into the blast furnace with the batteries. The blast air is preheated to 500°C. It is felt the use of whole batteries reduces the fuel (coke) requirements and also minimizes flue dust production.[51-54]

There is a direct smelting process which uses an electric furnace for smelting "whole" batteries. The batteries are crushed only, then burdened with a sodium/potassium carbonate mixture, limestone, iron chips and coke. The mixture is melted in an electric furnace at 1000-1100°C yielding a hard lead alloy, matte, slag and flue dust.[55]

Industrial Processes - Indirect Smelting

Indirect smelting of battery material is the pyrometallurgical processing of battery scrap after it has been mechanically classified. Usually the metallics are simply melted and the paste material treated with a reducing smelt but in some cases both are treated together to yield a hard lead of intermediate antimony content. Treating pastes together with metallics is generally only used where there is a readily available market for hard lead. For example, some battery manufacturers treat scrap this way in order to fulfill their hard lead requirements. After smelting (most commonly in a rotary furnace), more antimony is added to bring the antimony content to the desired level. The lead is then used for casting grids, bars and posts. This manufacturer must look to the market place to obtain soft lead for making the lead dioxide for the new batteries.[56]

There are two options available in smelting battery scrap, a one stage or a two stage smelt. A one stage smelt is accomplished by smelting the material under strongly reducing conditions. This reduces the lead and antimony producing a hard lead alloy and a relatively clean slag. (If only pastes are smelted, the alloy will have a low antimony content but if metallics are included in the smelt the alloy will have an intermediate antimony content.) In the two stage smelt, the material is first treated to an oxidizing smelt which yields virtually pure lead and a slag rich in antimony and lead. The second stage, performed under strongly reducing conditions, produces an alloy high in antimony and a discardable slag. Thus depending on the types of alloys an operator wishes to obtain, he has the choice of smelting metallics separately or with the paste with either a one or a two stage smelt.[57-59]

The short bodied rotary furnace is becoming very popular with scrap battery processors, especially the smaller operators. This furnace is ideal for both one and two stage smelting.[60] It is less costly, both in capital and operating terms, more versatile (can treat different concentrates) and easier to operate than the lead blast furnace. There are many papers and patents in existence on the operation of and fluxing practices with rotary furnaces for smelting of lead concentrates (all of which tend to be variations of "conventional" smelting procedures).[61-69]

Commercial Operations

Penarroya of Trappes, France is replacing their blast furnaces with the more versatile rotary furnaces for processing battery scrap. They are versatile in fuel requirements (can be fired by gas, oil or pulverized fuel), batch operations enable different materials or charges to be used depending on the material to be smelted and its thermal inertia and rapid emptying and fill capabilities allow for shut downs with a minimum loss of productivity. A charge for the furnace consists of the lead-bearing material, soda ash, iron chips, sand if silica is necessary and anthracite coal for a reductant. Productivity of the plant was increased by premixing charge material, mechanization and automation of taphole drilling, installation of more efficient burners and pelletization of flue dust.[5]

Simsmetal Pty. Ltd. of Australia has an operation almost the same as **Penarroya.** Like **Penarroya, Simsmetal** found blast furnace smelting of whole batteries to be metallurgically inefficient, environmentally difficult and only marginally profitable. Thus they began breaking batteries and treating in a rotary furnace. Operation of the smelter, charge preparation etc. is the same as described for **Penarroya.**[70]

Instead of a short rotary kiln, **N.L. Industries** in New Jersey, U.S.A. has modified a used cement kiln for smelting batteries. Metallurgically, the operation is similar to the short rotary furnace, except the length of the kiln (54 m) allows for continuous charging (although tapping is intermittent) and for higher feed rates (due to the longer residence time). As with shorter furnaces, fluxes are soda ash and cast iron chips and coke is the reducing agent.[15]

RSR Corporation of Texas uses a reverberatory/blast furnace combination for smelting battery scrap. The battery scrap is treated in three distinct smelting operations. The first two operations are performed in the reverberatory furnace. In the first smelt, virtually all of the antimony is oxidized, producing a pure lead bullion. The slag is then rerun through the reverberatory furnace with a carbon reducing agent to produce a low antimony bullion. The final slag is processed in the blast furnace under strongly reducing conditions to yield a high antimony lead bullion (15-25% Sb). **RSR** uses these metals in the production of various alloys.[16]

Stolberger Zinc A.G. uses only a blast furnace, feeding paste residues with its lead sinter from primary lead operations. The metallics recovered by their mechanical processing plant are melted separately.[13]

The smelting of battery paste in electric furnaces has been described in a number of publications and patents.[35 37] As with other processes, the pastes are mixed with a silica/limestone/iron flux and a coke reducing agent and then fed into the furnace.[71-74] Another patent describes the use of a $CaO/CaF_2/SiO_2$ flux with reduction performed in an induction furnace.[75] **Liniger**[76] describes this method, with anhydrous carbon as a reductant, in order to minimize the production of offgas. This allows for a smaller offgas filtering system and produces a high SO_2 offgas amenable to SO_2 recovery through compression.

A unique process is used by **Bleiberger Bergwerks Union** in its battery processing facilities. The metallics are melted in a rotary furnace because small amounts of entrained casings produce smoke and it also allows them to reduce the dross produced by entrained paste material. The paste fraction from mechanical processing is smelted in the BBU rotary hearth furnace. The furnace consists of an annular ring hearth, the basin of which is refractory lined except for the inside wall (against the hub) which is water cooled. The ring itself rotates around the hub at approximately 1/3 rpm. At one point a mechanical poker stirs up the mass as it goes by, stoking the charge up against the inside wall. Ore, battery paste and coal are charged continuously just in front of the poker, and air is charged into the hearth (all around) through the hub. The charge in the hearth is kept in a "pasty" condition. The slag rolls down to the outside of the ring where it is removed and metallic lead settles down through the charge to the bottom of the hearth where it is intermittently tapped. The net result of this process is that material of 70% lead is beneficiated to 98% lead. Feed is restricted to high lead content material (minimum of 70% lead) and there are high losses to the slag (the slag is approximately 39% lead). The advantages of the rotary hearth process are the low cost of equipment, low grade fuel used, low fuel requirement, versatility in that any high lead content material can be processed (without sintering), no fluxes are used, startup and shutdown are fast and simple and personnel requirements are low.[12, 77, 78]

Process Improvements and New Processes

The economics of any process is of primary importance and, to this end, work is constantly being done on improving and optimizing existing processes or developing new ones. A major area of optimization is the flux composition of charges for pyro-reduction.[79-83] Cheaper material can replace some fluxes in some operations such as clinker from rotary kiln processing for Fe and C;[84] or iron ore instead of galena in the shaft furnace to improve charge permeability.[85] Another substitution, used by some operators, is the replacement of lime with chalk[49] which is not only cheaper but can result in increased output.[86] Other process alterations include oxygen enrichment of the air blast[87] and heat treating the pastes with tars or oils to carburize them prior to charging to the furnace (so that they are "self reducing").[88]

There are various new processes which have been developed with varying degrees of success. Top blown rotary furnaces have been given some attention.[89] With this furnace, fluxes, recycled flue dust and concentrates can be pneumatically charged. The initial (oxidizing) smelt produces bullion and a 45-50% lead slag. The lead in the slag is reduced by charging coke breeze through the lance. The final slag contains 1-2% lead.

Another new process involves injecting -100 mesh battery paste into a conduit with air, a reducing gas and oxygen. The mixture leaves a nozzle, ignites in a furnace and the molten metal and slag fall from the flame and are separated in the furnace hearth.[90]

A few attempts have been made with contacting the battery material with a molten bath to reduce the lead compounds. The batteries are first comminuted, the organics present serving as a reducing agent. The bath can be molten alkali metal carbonate salt[91] or molten lead.[92] Results from this type of processing were generally not very satisfactory.

Finally, reduction by heating battery material in the absence of air has been tried, in an effort to reduce offgas production.[93] This is usually done in electric furnaces, producing an offgas rich enough in SO_2 for recovery by compression.[76]

C. HYDROMETALLURGY

Literature on the full scale industrial use of hydrometallurgical processing was not found in this survey. Thus, it is assumed that at this time, hydrometallurgical processes are only in the research or pilot plant stage.

Hydrometallurgical studies have concentrated on two areas of processing battery pastes; desulphation of the battery pastes and complete hydrometallurgical recovery. Desulphation uses a hydrometallurgical step to remove the sulphur from the $PbSO_4$ to reduce SO_2 production during subsequent smelting. Generally, with complete hydrometallurgical recovery, the lead compounds are dissolved in a solution and electrowon as pure lead or precipitated as a saleable lead compound.

Paste Desulphation

Much work has been done on desulphation of battery pastes. The advantage of removing sulphur hydrometallurgically is that no equipment is necessary for the recovery of SO_2 from the smelting offgases. The general desulphating process involves slurrying the battery pastes in an aqueous solution which converts the $PbSO_4$ to PbO or $PbCO_3$. The lead compound is then filtered and treated by pyro-reduction (with or without calcining). Depending upon the chemical used, the sulphate is either left in the aqueous phase or is precipitated as some other sulphate. If aqueous, the sulphate is removed in the filtration. If present as a precipitate, the sulphate compound enters the pyro-reduction step along with the lead. In this case, it is essential that the sulphate form a stable matte (sulphide) in the melt.

Those solutions which form aqueous sulphates are ones of sodium carbonate[94-96] and ammonium carbonate.[97-102] These solutions yield $PbCO_3$ which can be smelted directly or calcined to PbO. Calcium hydroxide is the other reagent which has received attention, forming $CaSO_4$ and $Pb(OH)_2$. When the calcium sulphate precipitate is smelted along with the lead compound, calcium sulphide is formed which is stable in the pyro-process.[103-105] In an exhaustive study of this process by the USBM, the precipitate was smelted with a NaCl/KCl flux and carbon reductant at 650°C. The flux could then be recovered from the slag with a water leach.[106]

In a related patent, the filter cake from a $Na_2CO_3/PbSO_4$ mixture is slurried with HNO_3, then filtered to produce an aqueous $Pb(NO_3)_2$ solution.[107]

The only "industrial" use of hydrometallurgy encountered in this survey was in the area of desulphation. **RSR Corp.**, in an expansion of their battery processing facilities, included a pilot plant desulphation operation using ammonium carbonate.[16]

Hydrometallurgical Processes

In complete hydrometallurgical recovery, many different reagents and processes have been investigated. These can be broadly classified as lead chloride production for fused salt electrolysis, alkali leaches, ethylene-amine leaches, ammonia leaches, direct electrowinning and other miscellaneous processes.

To produce lead chloride, the crushed scrap is vigorously agitated with a $NaCl/HCl/H_2SO_4$ leach liquor at 170°C to dissolve the lead compounds. The lead alloy is separated, then $PbCl_2$ is crystallized from the leach liquor. Lead is produced from the $PbCl_2$ by fused salt electrolysis.[108] Alternatively, lead can be recovered directly from the leach liquor by reaction with electrolytic manganese,[109] or the $PbCl_2$ crystallized, melted and reduced with hydrogen.[110, 111]

Leaching of the lead compounds from crushed scrap can also be accomplished with aqueous solutions of potassium or sodium hydroxide. The leaching solution is generally quite alkaline (1-7 M) and sugar, molasses or tartaric acid is added to promote dissolution. The lead is then electrowon from solution.[112-119]

The most complete alkali leach process was developed by the **Institute of Technical Physics** of the **Swiss Federal Institute of Technology** and is called the *PLOMBREC SYSTEM.*[1] In this process the lead compounds are dissolved and plastics and metallics removed in a rotating "leaching drum" (solution 20% NaOH, 200 g/l sugar and temperature 80°C). The metallics are separated from the plastics in a sink/float process. The leach solution contains sodium sulphate and lead hydroxide. The SO_4 is removed and the NaOH regenerated by cooling and adding KOH (SO_4 precipitates as K_2SO_4 which is used as fertilizer). Finally, the lead is electrowon in a cascade cell (20 A/dm^2, current efficiency up to 75%) reducing the lead concentration from approximately 200 to 30 g/l. The lead sponge produced is run through a compacting press to remove much of the remaining lye.

The third type of reagents used are ethylene/amine solutions, notably ethylene diamine and diethylene triamine. These have mainly been studied in the leaching of PbO with ethylene diamine sulphate or diethylene triamine sulphate solutions (i.e., amine + H_2SO_4). The lead is precipitated from solution as $PbCO_3$ which is then calcined to Pb_3O_4.[120-124] Alternatively, diethylene triamine can be used with HCl to leach PbO, precipitation of Pb(OH)Cl being accomplished with H_2SO_4.[125] Another paper advocates the use of triethanolamine solutions instead of ethylene amine solutions.[126] Generally, the amine solution is regenerated.

Although studies have shown that the highest lead concentrations could be obtained with ammoniacal ammonium nitrate solutions,[127] ammoniacal ammonium sulphate solutions have more popularity in the literature.[128] [129] In ammoniacal ammonium sulphate solutions, the solubility of lead sulphate increases with increasing concentrations of free ammonia (NH_4OH) and ammonium sulphate, most likely dissolving as $[Pb(OH)SO_4]$. Lead oxides are soluble except for lead dioxide. The dissolution rate is virtually independent of temperature and solution concentration; a maximum lead concentration is achieved after about five minutes of agitation.[122] Lead is recovered from the solution by electrowinning or precipitation. Electrowinning produces lead at the cathode and lead dioxide at the anode. Precipitation of the lead can be achieved by removal of free ammonia through heating or steam distillation (producing lead ammonium sulphate, monobasic lead sulphate or a mixture of the two), cementation with various metals, hydrogen reduction, precipitation with CO_2 or H_2S, dilution with water or neutralization with H_2SO_4.[130] [131] Another possibility is to adsorb the lead onto coal or coke and then recover it by oxidizing the carbon.[132]

In some processes, acids are used to dissolve the lead which is recovered by electrowinning. For acid dissolution, the sulphate must first be removed by low temperature reaction with aqueous KOH, NaOH or $(NH_4)_2CO_3$. The lead oxides or carbonates produced are then dissolved in H_2SiF_6,[133-135] HBF_4[136-141] or alkanesulfonic acid[142] and subsequently electrowon. In such electrowinning, lead dioxide production at the anode can be reduced by phosphorous[135] or arsenic[143] additions to the electrolyte.

Some work has also been done on directly "electrorefining" scrap (metallics and compounds together). A cell is used which holds the scrap in some sort of conducting basket as the anode. A NaOH or KOH electrolyte is used with current densities up to 10 amps/sq dm.[144-146] Pure lead is plated out at the cathode while the hard lead remains at the anode. In a variation on direct electrolysis, batteries are charged, the bottoms removed and the entire battery is immersed in an electrolytic cell. By connecting one lead from a DC power source to both battery terminals, the insides of the battery become the anode, the lead dissolves into the tank of electrolyte and is plated out on a separate cathode.[147-152] Another process has the lead compounds sandwiched between a cathode and anode for reduction in an H_2SO_4 electrolyte.[153]

There are a few other processes which have been investigated in hydrometallurgical processing. One uses a gluconate anion to complex the lead from $PbSO_4$. The lead is then recovered in an electrolytic cell in which anodic H_2SO_4 and cathodic $PbSO_4$ are separated by an anion exchange membrane; H_2SO_4 and Na_2SO_4 are recovered as byproducts.[154] Another process uses a $FeCl_2$ solution to selectively leach PbO_2.[155] Lastly, two novel processes can be used to produce $PbCO_3$. The first uses an NaCl leach, then $PbCO_3$ is precipitated with solvay soda.[156] The second uses an $(NH_4)_2CO_3$/AcOH leach to produce a lead acetate solution from which $PbCO_3$ is precipitated with gaseous CO_2.[157]

III. PROCESS SELECTION

Using the information provided in the literature, the desirability of any one process can be evaluated through comparing which aspects of the process are favourable and which should be avoided. This in turn is determined by studying the problems encountered with current processing methods. Problems with the process itself are generally solvable, due in part to the large reservoir of technology available from the primary lead industry. Environmental concerns, however, are having an impact which is most difficult to avoid with the processing technology in use today.

Process Problems

In mechanical processing, the heterogeneity of feed material (i.e., different types of batteries with different constituent materials) is no longer a problem with the use of large shears and efficient separation plants. With most processes, the operating parameters can be altered enough to accommodate the different types of batteries. Generally, inefficiencies in mechanical separations (such as small metallics being recovered and smelted with the fines rather than being simply melted with the rest of the metallics) can be tolerated to a great extent and have little effect on the overall economics. If the plastic case material is to be recycled, some difficulty may be experienced with lead materials adhering to the plastics. Generally, a separate washing step is used to correct this problem.

In pyrometallurgical processing, few problems with the processing itself are experienced in modern smelters. Some difficulty may be experienced by operators when their process cannot adapt quickly to changes in the marketplace (for example, if they can only produce hard lead when there is a premium on soft lead). Another problem has been the increasing use of PVC for separators in batteries. The PVC forms $PbCl_2$ in the furnace which, because of its volatility, will build up in the flue dust by continuously recycling. For operators experiencing this problem, consideration must be given to removing the separators prior to smelting (i.e., mechanical processing) or finding a way of handling or treating the flue dust other than returning it directly to the furnace.

Problems with hydrometallurgical processes are as yet unknown because they are not being used commercially. Research tends to concentrate on a specific area or problem in a process, meaning general problems with the overall process are not encountered.

Battery Processing: Environmental Concerns

By far the most important problems facing battery recyclers are environmental issues.[158] These problems can be classified into three main categories: process emissions, in-plant hygiene and battery handling.

Process emissions include the lead dust emitted by smelting operations, SO_2 produced in the reduction of $PbSO_4$ and lead contaminated water from mechanical processing operations. Generally, lead dust emissions are controlled with bag-house filtration and SO_2 emissions with sulphuric acid plants (in larger operations) or with simply diluting the exhaust gases to lower the SO_2 concentration (in smaller operations). In mechanical breaking and sorting operations, the process water is generally recycled. For water which must be disposed of, pH adjustment and settling are usually effective to achieve satisfactory lead concentrations. Thus, the technology is available to control process emissions, but keeping up with and complying with ever changing environmental regulations demands substantial time and financial effort from battery recyclers.

In-plant hygiene was the major problem for smelters in the early 1980's when OSHA in the United States imposed a lead-in-air maximum of 50 micrograms/cubic meter of air. Many processors found they could not bring their lead-in-air in the work environment much below the previous 150 micrograms/cubic meter limit by installing larger fume hoods and exhaust fans.[159] This regulation by itself forced the closure of many battery smelting operations.

The environmental problems of the late 1980's now center around the implementation of hazardous waste regulations and handling of the batteries themselves. Used lead-acid batteries are now classified as hazardous waste in the United States. This has major implications in how batteries are stored and transported and also requires from the processor, compliance with special licencing and insurance regulations. Byproducts from processing also become hazardous waste, complicating disposal of such things as furnace slag. Another consequence of the EPA's activity in this area is the "superfund" assessments made to processors who remain in business. The "superfund" is a pool of money obtained from businesses in a particular activity (in this case battery breakers and smelters) to pay for clean-up of contaminated plant sites left by bankrupt businesses in the same activity.[4,60] As fewer and fewer businesses are saddled with the financial responsibility to clean up the sites of more and more businesses which fail, these superfund assessments become completely disproportionate to the scale of the operations remaining in business.

Even in areas where regulations are much more lenient, such as Alberta, the tightening of environmental regulations is being felt. Hazardous waste laws implemented in 1988 complicate the disposal of waste H_2SO_4 from batteries (although in Alberta used batteries themselves are not yet classified as hazardous waste). Another example of the growing concern of environmental regulators for lead pollution was the issuance of clean up orders by Alberta Environment to all the battery breaking operations in Alberta. Even the Air Quality Branch was involved in this clean up order, concerned that lead dust left on the ground at these sites would get into the air from wind, vehicle traffic, etc.[16]

The AAS Process

The AAS or ammoniacal ammonium sulphate process was chosen for further development, building upon the work of Bratt and Pickering.[30] In this process lead sulphate, lead ammonium sulphate, monobasic, dibasic and tribasic lead sulphates, lead monoxide and water soluble lead compounds can be leached with an aqueous ammonium sulphate solution containing free ammonia. Bratt and Pickering believed that the principal ionic species present in the lead bearing AAS solution was $[Pb(OH)SO_4]^-$, dissolution occurring by:

$$PbSO_4 + NH_4OH = NH_4[Pb(OH)SO_4]. \qquad (2)$$

The lead can then be recovered in a number of ways from the pregnant AAS; lead compounds can be precipitated by a number of methods, or metallic lead can be electrowon from the solution.

The initial design for the bench scale pilot plant is described in Chapter V; the objective was to combine the mechanical separation of the battery components in the same step with the dissolution of the battery pastes. The major components were a leach tank and an electrowinning tank. The leach tank was constructed so that the AAS solution flowed upwards through the tank, with the flow velocity decreasing with height in the tank (i.e., the cross-sectional area of the tank increased with height). This created a velocity regime in the tank such that metallics would sink to the bottom (to be removed), plastics and separators would be carried out of the tank by the solution flow and the lead compounds in the pastes would be held in suspension in the tank (at the point where their downward velocity relative to the AAS equalled the upward velocity of the solution) to be dissolved. The dissolved lead was to be recovered as metallic lead by electrowinning.

The AAS process has many potential advantages over other processing techniques, the most important of which are the environmental problems it solves. As the materials are always kept wet during processing, there is no chance of lead dust being produced. (The final process step for both lead from the metallics and from the pastes is simply melting, where emmissions are easily controlled.) Thus, the only chance of fugitive emmissions are AAS spills; these being liquid, however, are easily detected and cleaned up. Acid handling is eliminated as the AAS can be introduced at the battery crushing stage, where it will neutralize the acid immediately. Finally, $PbSO_4$ is reduced electrochemically, so sulphur emmissions are eliminated.

The plant design is quite simple, and the only extra equipment that would be needed in a commercial operation would be a shear to shred the batteries and furnaces to melt the final product. This simplicity will allow for a low capital investment to set up such an operation, making the process amenable to small scale operation (which would also result in savings in transportation of batteries to feed the operation).

The only inputs to the process are NH_3 to make up for the NH_3 consumed in the production of $(NH_4)_2SO_4$ (from both H_2SO_4 neutralization and $PbSO_4$ reduction) and electricity for the electrowinning. Both are reasonably inexpensive and readily available.

The products separated and recovered by the process are the plastics and separators (floated off the leaching tank), metallics from the grids and posts (sinks in the leaching tank), metallic lead from the electrowinning and $(NH_4)_2SO_4$ which must be crystallized out of the AAS. Thus, in addition to producing both hard and soft lead, the plastics can be recycled and the $(NH_4)_2SO_4$ is saleable as fertilizer.

Other advantages of the AAS process are that pastes suspended in the leach tank will act as a heavy medium to enhance the separation of the battery components. Also, by not using screens a better separation of the small metallics can be achieved; they will report to the "sinks" rather than to a "fines" fraction. The final plastics and metallics products should be cleaner than with other mechanical processing techniques, as pastes adhering to their surfaces can be dissolved by the AAS rather than relying solely on a physical separation. Finally, the materials handling can be easily automated and the system operates at normal temperature and pressure. This will help to lower labour and energy costs.

Even compared to the similar *Plombrec* process,' the AAS process demonstrates advantages. In the AAS process dissolution is accomplished at normal temperatures, eliminating the need to heat the solution as with the *Plombrec* process. Also, the separate step of sulphate precipitation is eliminated in the AAS process. Because of its value as a fertilizer, the conversion of battery acid to $(NH_4)_2SO_4$ in the system can be tolerated, while waste acid must still be handled separately in the *Plombrec* process (to avoid excessive NaOH comsumption).

The only problem anticipated with the AAS process is the insolubility of PbO_2 in the AAS. It is expected that the battery material can be pretreated with H_2SO_4 to convert the PbO_2 to $PbSO_4$. The $PbSO_4$-H_2SO_4 slurry from this treatment can then be fed directly into the system without solid/liquid separation.

It is hoped that this pilot plant study of the AAS process will develop a simple and effective self-contained operation for recycling scrap lead-acid batteries. While producing no byproducts which pose a disposal problem, the process should solve the environmental problems faced by today's commercial battery recyclers.

IV. PRELIMINARY EXPERIMENTS

A number of "preliminary" or "exploratory" experiments were carried out for a number of reasons. These experiments afforded some familiarity with the behavior of the reagents and materials used in the process as well as providing experience with the analytical methods used to evaluate it. As well, these experiments provided data for comparison to published results. Finally, and most importantly, they provided the necessary data to determine the type and size of equipment needed in the pilot plant design.

These experiments covered three major areas of the process. The first area was characterization of scrapped car batteries, i.e., the nature and proportions of the materials contained in the batteries. The second area was the leaching of the lead compounds with the AAS solution, including the conversion of lead oxides to sulphates by treatment with sulphuric acid. Thirdly, the electrowinning of lead from the pregnant AAS solution was explored.

Characterization of Scrap Batteries

To determine the relative proportions of the battery constituents (as well as to provide feed material for subsequent experiments), five automotive batteries were broken by hand and separated into case material, separators, metallics and fines (or pastes). The results for the five batteries are shown in Appendix I, Table 1.

The average battery weight was 17.7 kg when full and 14.6 kg when drained of electrolyte. There are two types of case material; hard rubber and polypropylene. The hard rubber cases were much heavier, therefore comprised a larger proportion of the batteries' weight. The constituent weights are averaged from three polypropylene cased batteries with the corresponding numbers for the two hard rubber cased batteries in brackets following. Case material averaged 0.99 kg (2.84 kg) or 6.7% (19.7%); the separators averaged .95 kg (.96 kg) or 6.5% (6.7%); the metallics averaged 3.22 kg (2.50 kg) or 21.9% (17.3%) and the fines averaged 9.54 kg (8.10 kg) or 64.9% (56.3%) of the battery's drained weight.

In a second breaking operation where 21 batteries were broken, the average drained weight was 17.8 kg and the constituent proportions were: case material 16.2%, separators 4.5%, metallics 45.6% and fines 33.7%. In this lot, there was a fairly large proportion of hard rubber cases. There was a large difference in the proportion of metallics and fines between the two breaking operations and this is attributed to the amount of grid material left in the "fines" constituent. The grids are very thin, brittle castings which break easily; when separating the fines it was rather arbitrary as to how much of the metallic grid material was separated from the "fines". It can be seen, however, that the total of metallics and fines are, in each case, close to 80% of the drained battery weight.

Metallics

The separated metallics from the former five batteries were dried and melted. The metallics lost 1.4% of their weight on drying and a further 6.3% upon melting. Thus, lead recovery from the metallics was 92.3% of the separated weight. Atomic absorption analysis indicated the recovered metal was approximately 4% antimony and 96% lead (some of the spongy lead from the negative plates ended up with the metallics; as it is pure lead, it would reduce the overall antimony content of the melt).

Fines

The separated fines were processed for feed material for the leaching experiments by drying and grinding. Drying indicated a moisture content of 12% for the fines. After drying, the fines were ground in a laboratory ball mill for approximately 1/2 hour per charge (5 kg). A sieve analysis is shown in Appendix I, Table 2.

The composition of the fines was determined by x-ray diffraction and the lead content was determined by fire assay. X-ray diffraction indicated that the fines were composed mostly of $PbSO_4$ with lesser amounts of PbO_2. Metallic lead did not show on the charts, being overshadowed by the much higher $PbSO_4$ and PbO_2 contents.

Two samples of the fines were taken by running the fines through a riffler. Twenty five gram samples were assayed by melting for 2 hours at 925°C under a monobasic sodium/potassium silicate slag containing 7 g of carbon reductant. These melts yielded lead buttons weighing 22.7 g and 23.1 g. Atomic absorption analysis showed these buttons to be approximately 1/2% antimony. Thus, the lead content of the fines was approximately 91% (which is in agreement with published figures[162]).

A. PRELIMINARY LEACHING EXPERIMENTS

Solubility of Lead Sulphate in AAS

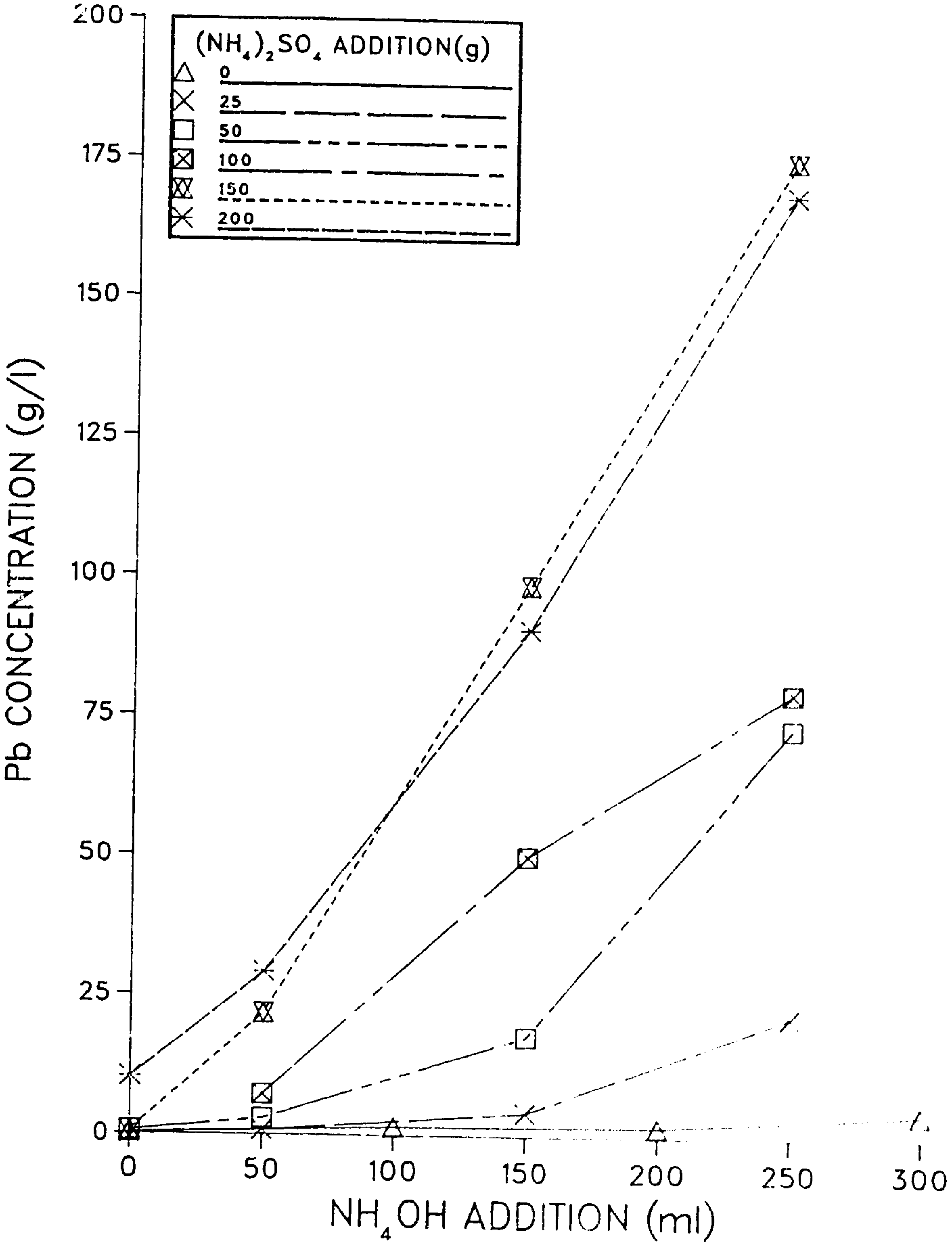
The first experiments were to determine the solubility of $PbSO_4$ in a range of AAS concentrations. These were done by agitating 40 to 100 g of reagent grade $PbSO_4$ (ensuring an excess of $PbSO_4$ in each test) in AAS solutions with various concentrations of NH_4OH and $(NH_4)_2SO_4$. Both the NH_4OH and $(NH_4)_2SO_4$ were reagent grade and the agitation was provided by an overhead stirrer. For each NH_4OH and $(NH_4)_2SO_4$ combination, the experiment was carried out for 21 minutes. The stirrer was shut off for one minute before each sample was taken for analysis, to allow the undissolved $PbSO_4$ to settle. Thus, samples were taken at 2, 4, 6, 11, 16 and 21 minutes, recorded as 1, 3, 5, 10, 15 and 20 minutes of leaching, respectively.

The NH_4OH concentration used in each run was made by mixing a specified quantity of reagent grade NH_4OH with enough water to make a total of 300 ml. A specified weight of $(NH_4)_2SO_4$ (granular) was then added to the diluted NH_4OH. Thus, the AAS concentration for each run is designated by three numbers; for example 50:250:100 indicates 50 ml of concentrated NH_4OH, 250 ml of water and 100 g of $(NH_4)_2SO_4$. The results are described according to the initial makeup of the AAS solution; no analysis was done to determine the final NH_3 or $(NH_4)_2SO_4$ concentrations. These final concentrations cannot be calculated from the initial makeup of the AAS solution for a number of reasons. The final concentrations are affected by the evaporation of NH_3 from the solution and the effect the $(NH_4)_2SO_4$ addition has on the total volume of solution. Also, with large $(NH_4)_2SO_4$ additions not all the $(NH_4)_2SO_4$ dissolves; the $(NH_4)_2SO_4$ and $PbSO_4$ dissolution are interdependent (i.e., the capacity of the AAS to dissolve $(NH_4)_2SO_4$ increases with $PbSO_4$ dissolution).

The range of concentrations explored were from 0 to 300 ml NH_4OH (i.e., approximately 0 to 247 g/l NH_3) with from 0 to 250 g $(NH_4)_2SO_4$. The results are shown in Appendix I, Table 3 and summarized in Figure 1. It can be seen that the $PbSO_4$ solubility increases with increasing NH_3 concentration and, for a given NH_3 concentration, with increasing $(NH_4)_2SO_4$ concentration.

With higher NH_3 concentrations, the advantage of higher lead concentrations is offset by higher NH_3 evaporation losses. Thus, a middle range NH_3 concentration, which provides an "adequate" lead concentration, would be best for leaching. The chosen AAS concentration for subsequent experiments was the 150:150:150 AAS solution which is

FIGURE 1. SOLUBILITY OF LEAD SULPHATE IN AAS.



hereafter referred to as the "standard AAS solution".

Lead Dioxide Leaching

PbO_2, being the second important compound in the battery fines, was leached in standard (150:150:150) AAS solution to determine its solubility. Seventy five grams of reagent grade PbO_2 was stirred in the AAS for five minutes then let stand for 55 minutes to allow the fine PbO_2 to settle. The lead concentration was 0.36 g/l, which indicates that PbO_2 is virtually insoluble in AAS.

Sulphuric Acid Pretreatment

As PbO_2 is a major constituent of the battery fines and is not soluble in AAS, it would be useful to be able to convert the PbO_2 into soluble $PbSO_4$. It is this reaction which provides the power in a battery, so it was anticipated that few problems would be encountered in effecting the conversion. It is desirable to make this conversion in as weak an H_2SO_4 electrolyte as possible so that in a commercial process the electrolyte from the batteries could be used as the H_2SO_4 source. Thus, 50 g samples of battery fines were slurried in 250 ml of 271 g/l and 706 g/l H_2SO_4 (these concentrations representing the electrolyte H_2SO_4 concentration for a fully discharged and a fully charged battery, respectively). Four trials were run: 10 minute treatment in 271 g/l H_2SO_4, 10 minutes in 706 g/l H_2SO_4, 12 hour treatment in 271 g/l H_2SO_4 and 5 hours in 706 g/l H_2SO_4

(the last being a sample from "Sulphuric Acid Pretreatment: Feed Preparation", described in the next experiment). At the end of the pretreatment time, the samples were drained, rinsed with water and dried. 20 g from each sample was then leached in standard AAS for 10 minutes (five minutes of stirring, followed by 5 minutes settling). A control sample was not treated with H_2SO_4.

The results are shown in Appendix I, Table 4. The H_2SO_4 pretreatment resulted in a slightly higher solubility of battery fines in the AAS, the best result being a 15% increase in solubility for 10 minutes in 706 g/l H_2SO_4. X-ray diffraction for all the samples still showed a mixture of $PbSO_4$ with small amounts of PbO_2. There was little difference in the x-ray diffraction patterns for all five trials.

Sulphuric Acid Pretreatment: Feed Preparation

To prepare battery fines for subsequent leaching tests ("Solubility of Battery Fines in AAS"), 1000 g of fines were slurried in 500 ml of 706 g/l H_2SO_4 for five hours with mild agitation. The material was then washed and decanted (to remove the H_2SO_4), dried and ground. A sample was used for comparison in the previously described experiment.

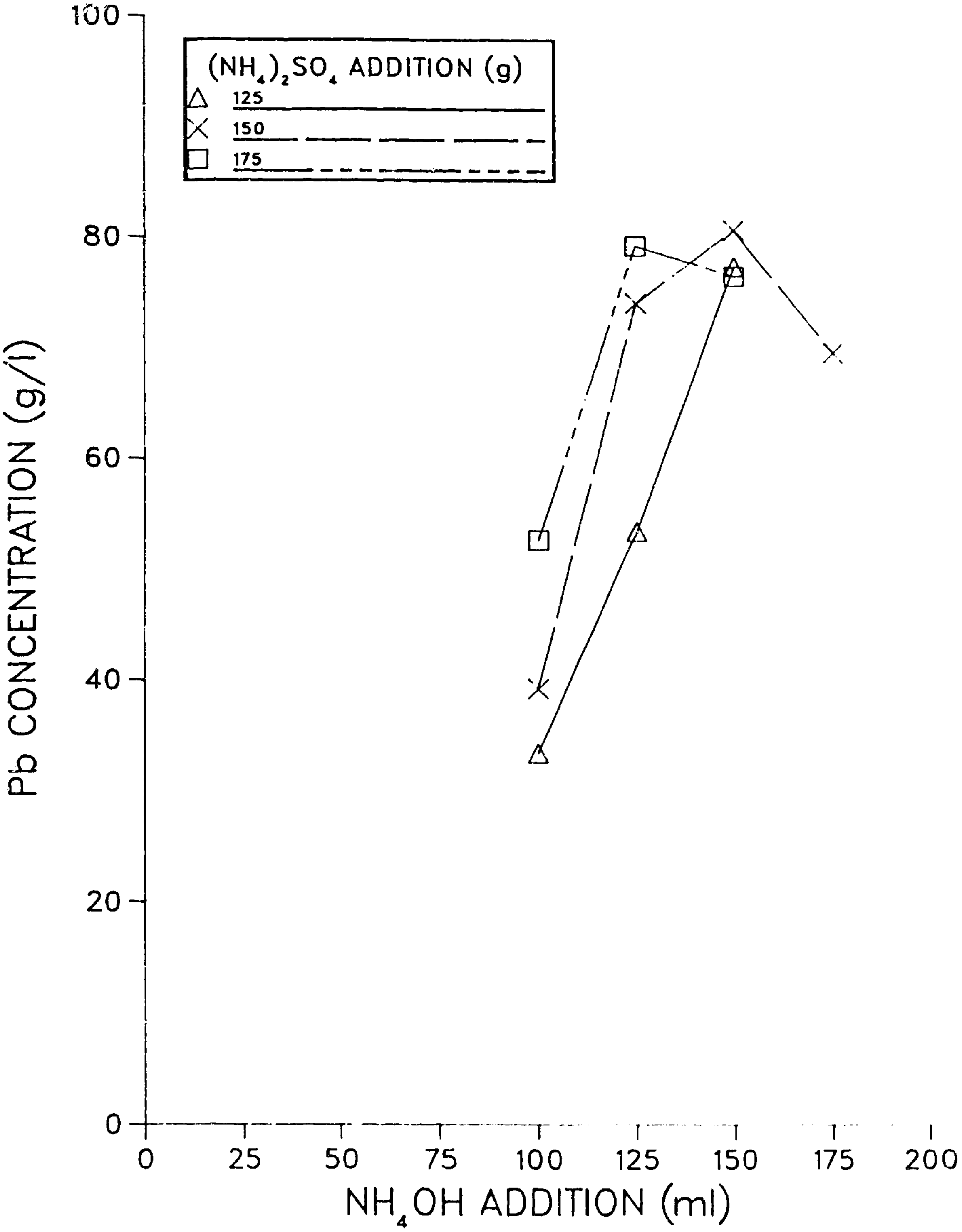
It is interesting to note that after H_2SO_4 pretreatment, the 1000 g of fines weighed 1015.8 g. This would indicate an increase in $PbSO_4$ content from 56.1% (control, previous experiment) to 62.5%. The leaching test, however, [illegible]ed a 59.0% $PbSO_4$ content.

Solubility of Battery Fines in AAS

The second series of leaching experiments followed the same procedure and used the same apparatus as for the "Solubility of Lead Sulphate in AAS" experiments. In this case, however, battery fines that had been pretreated with H_2SO_4 in the last section were used in place of the reagent grade $PbSO_4$. Also, *Sherritt* untreated $(NH_4)_2SO_4$ was used, but the NH_4OH was still reagent grade.

For this set of experiments a narrower range of AAS compositions was used; $(NH_4)_2SO_4$ additions were between 125 g and 175 g and NH_4OH concentrations were between 100 ml and 175 ml diluted to 300 ml. The results are shown in Appendix I, Table 5 and summarized in Figure 2. The reliability of the values shown here is questionable; however, the general trends indicated are believed to be representative. As the $PbSO_4$ in the fines dissolved, the solution became steadily darker. The reason was that the $PbSO_4$ and PbO_2 are intimately associated. As the $PbSO_4$ dissolved, the fine PbO_2 was released to remain suspended in the solution and was very slow to settle out (the one minute that the stirrer was shut off before taking a sample was not enough). Thus, the samples contained not only lead from the dissolved $PbSO_4$, but also from the PbO_2 in suspension. In two of the runs, a 20 minute sample was not taken. Instead, the stirrer was shut off at 15 minutes and the solution left

FIGURE 2. SOLUBILITY OF PRETREATED BATTERY FINES IN AAS.



to settle for 20 minutes. Samples of this clarified solution showed lead contents 34% and 42% lower than the 15 minute values.

Combined Sulphuric Acid Pretreatment and AAS Leach

In a commercial AAS process, H_2SO_4 will be fed into the system (the battery electrolyte) to be neutralized by the NH_4OH. If battery fines are pretreated in H_2SO_4, they could also be fed directly from the pretreatment into the leach process with the pretreat acid being consumed in the same manner as the battery electrolyte.

The effectiveness of feeding pretreated fines with acid directly into the AAS process was investigated in two sets of experiments. In both sets of experiments, 25 g of ground battery fines were pretreated in 72 ml of 706 g/l H_2SO_4 (corresponding to the H_2SO_4 content of fully charged battery electrolyte). When the pretreat time was completed, 296 ml of NH_4OH was slowly added to the fines/acid slurry. Finally 78.5 g of $(NH_4)_2SO_4$ was added and a sample taken for analysis after 5 minutes of stirring. The solution produced this way was equivalent to a 227:92:150 AAS solution.

The first set of experiments investigated pretreatment times on the solubility of the fines. The results were as follows:

Table 1. Effect of H_2SO_4 Pretreat Time on Battery Fines Solubility.

PRETREAT TIME (min)	Pb CONCENTRATION (g/l)
0	26.7
1	29.1
10	26.4
30	29.5
60	30.6
180	25.3

It can be seen that the results are scattered, showing no definite trend. The conclusion that was drawn from this experiment and from the previous H_2SO_4 pretreat experiment was that the H_2SO_4 pretreatment had very little effect in converting the PbO_2 into $PbSO_4$. In the energy producing reaction of a battery (equation 1), metallic lead is also involved in the conversion reaction to $PbSO_4$. Thus, in the second set of experiments 10 g of metallic lead powder was added to the 25 g of battery fines. Pretreat times of 10 minutes and 60 minutes were examined with the fines and lead stirred over the pretreat time (for greater exposure to the H_2SO_4) and for the fines left static over the pretreatment time (to allow better electrical contact between the fines and the lead powder). Also two controls were used; fines pretreated without the metallic lead powder addition and 10 g of lead powder without battery fines. The resulting lead concentrations (g/l) were:

Table 2. Effect of Lead Powder Addition on H_2SO_4 Pretreat.

	10 min	60 min
25 g fines + 10 g Pb powder (no stirring)	28.1	24.6
25 g fines + 10 g Pb powder (stirred)	25.8	30.1
25 g fines only	26.4	30.6
10 g Pb powder only	0.5	0.7

Again the data are scattered and show no definite trend.

The experiments in H_2SO_4 pretreatment were discontinued at this point. In the operation of the pilot plant, however, H_2SO_4 pretreatment was performed for some of the runs when it was found from Toguri's work[1,3] that the PbO_2 to $PbSO_4$ conversion was effective when performed at elevated temperatures.

Multiple Leaches

As it was anticipated that the pilot plant would be operated as a "steady state" system (i.e., solution continuously circulated between leaching and electrowinning, with the lead removal by electrowinning balancing the lead dissolution), the leaching was simulated by performing multiple leaches to determine the solvent effect of fresh solution on undissolved material and also to determine the total solubility of battery fines in AAS.

Seventy five grams of battery fines were treated in five consecutive leaches using standard AAS solutions. Each leach consisted of 5 minutes of stirring followed by 10 minutes of settling. The solution was then sampled and decanted, then fresh AAS solution was added to the undissolved fines for the next leach. The results were:

Table 3. Multiple Leaches.

LEACH	Pb CONCENTRATION (g/l)
1	56.0
2	22.8
3	8.1
4	5.3
5	3.8

The total volume from all five leaches was 1668 ml assaying 18.1 g/l lead. Therefore, 44.19 g $PbSO_4$ dissolved, constituting 58.9% of the original feed.

AAS Recycling

This test was performed to see how readily the AAS solution could be recycled to leaching from electrowinning. Seventy five grams of battery fines were leached in 350 ml of barren standard AAS from the electrowinning experiments (Chapter IV B). The slurry was stirred for 5 minutes, then allowed to settle for 10 minutes. The barren AAS assayed 7.75 g/l lead and after leaching contained 23.52 g/l lead. Thus, it was concluded that the AAS solution can be readily recycled from electrowinning to leaching.

B. PRELIMINARY ELECTROWINNING EXPERIMENTS

Apparatus

Preliminary electrowinning tests were performed using two mild steel electrodes clamped so they were suspended in clarified AAS solution in a 1000 ml beaker. The voltage was impressed upon the electrodes using a D.C. power source. An ammeter was connected in series in one electrode lead and a voltmeter was connected in parallel with the electrodes. An overhead stirrer was used to agitate the solution; the shaft ran between the electrodes and the impeller was below the electrodes.

Voltage Scans

These experiments were done to evaluate the current density which would be obtained with a certain electrode spacing and voltage. This information was used to narrow down the range of trials in subsequent electrowinning tests as well as to help in sizing the electrowinning apparatus to the leaching apparatus in the pilot plant design.

Approximately 680 ml of standard AAS solution was made up by twice mixing a 150:150:150 AAS solution with excess $PbSO_4$ (reagent grade) for 5 minutes, then decanting the solution into the 1000 ml electrowinning beaker. Six different electrode spacings were investigated: 1.5 cm, 2.5 cm, 3.5 cm, 4.5 cm, 5.5 cm, and 6.5 cm. For each electrode spacing the voltage was increased stepwise, stopping at each level and allowing the system to equilibrate for two minutes before the amperage reading was taken. The voltages tested were 1.3, 1.5, 1.7, 1.9, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, and 5.0. Samples for lead analysis were taken at the beginning of each run, after the 2.0 V reading and after the 5.0 V reading. For the 1.5 cm spacing two tests were done; one with a high lead concentration AAS (60 g/l) and another with a lower lead concentration (25 g/l). In all tests agitation was mild; that is, the stirrer was run on its lowest setting. The nominal electrode area (for current density calculations) for each test was readily determined by measuring the area over which the lead had plated. The results are shown in Appendix I, Table 6 and illustrated in Figure 3.

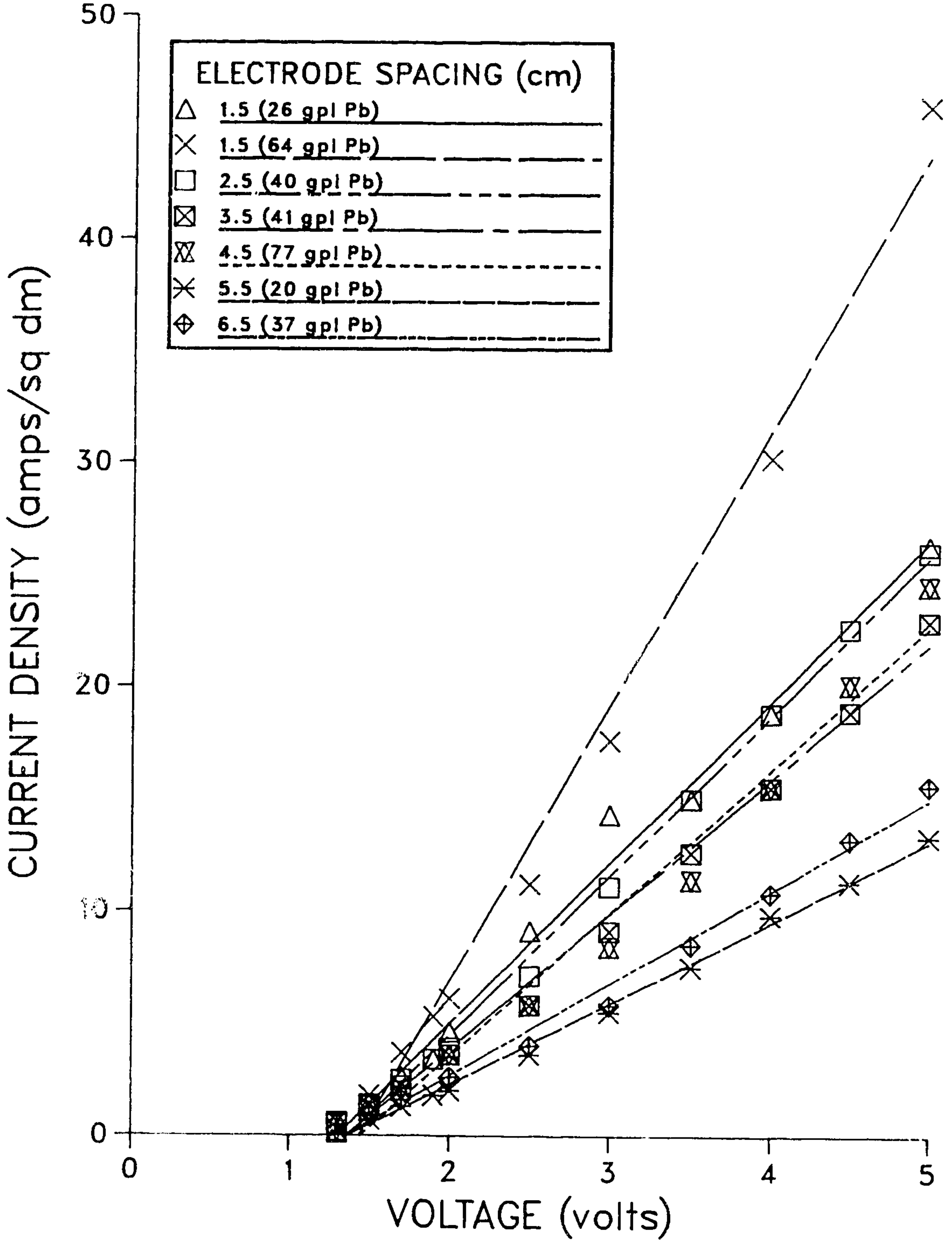
In all cases the cathode deposit was very spongy and readily fell off the cathode. Also, after approximately 3 volts, gassing occurred at the anode and a white precipitate formed in the solution.

Lead Electrowinning

These experiments investigated the effect of voltage, electrode spacing and agitation rate on current density and current efficiency.

The apparatus was the same as that used for the voltage scans. The clarified, leaded AAS, however, was solution saved from the leaching experiments. For each test, the measured variables were current and AAS lead concentration.

FIGURE 3. ELECTROWINNING CURRENT DENSITY.



The voltage, electrode spacing and agitation were all held constant through each test. Each test was performed for 30 minutes; the amperage was recorded every three minutes and samples for lead analysis were taken before the start of electrowinning and every six minutes during the run. The eight runs performed, along with the resulting current density and current efficiency, are shown below:

Table 4. Electrowinning Trials.

RUN	ELECTRODE SPACING (cm)	VOLTAGE	AGITATION RATE	CURRENT DENSITY (amps/sq dm)	CURRENT EFFICIENCY (%)
1	2.5	4.5	low	28.0	-
2	2.5	4.5	high	28.7	60
3	2.5	3.0	low	12.9	33
4	5.0	4.5	high	16.5	79
5	2.5	2.2	low	6.9	67
6	5.0	3.0	high	8.4	73
7	2.5	1.7	high	3.3	48
8	2.5	1.7	low	2.8	64

For the low agitation rate, the stirrer was run at its lowest setting and for the high rate, the stirrer was set as high as it could go without spilling the AAS solution. The data obtained are shown in Appendix I, Table 7.

For the current efficiency calculations, the weight of metallic lead after melting was used. This way $(NH_4)_2SO_4$ or lead oxides entrained in the wet cathode deposit were not mistaken for metal. This may lead to some negative error, however, as some oxides formed in electrowinning may have consumed lead metal during the melting (i.e., $PbO_2 + Pb = 2PbO$). This is believed to be the reason that no cathodic lead metal was recovered in Run 1.

As expected, current density was mainly a function of voltage and electrode spacing (current density increasing with higher voltage and smaller electrode spacing). Factors which improved current efficiency were lower current density, higher AAS lead concentrations, higher agitation and larger electrode spacing.

Generally, current density is considered the primary factor affecting current efficiency. In these experiments, lower current densities did increase current efficiency at low agitation rates; however, at high agitation rates the opposite occurred. The likely explanation for this anomaly, is that the AAS lead concentration was significantly higher for the (higher current density) runs where higher current efficiencies were experienced. Thus, in these experiments, it appears that the effect of lead concentration is at least as important as the current density employed. Larger electrode spacing and higher agitation rates also boosted current efficiency, but their effects were far less important than those of current density and AAS lead concentration.

Anode Deposit

X-ray diffraction showed the anode deposit to be PbO_2. For all but the lowest current density, the quantities produced were very small. It appears that the anodic current efficiency, with respect to PbO_2 production, was low (except at very low current densities). This is in apparent contrast to Bratt & Pickering's work[130] where it was suggested that lead be recovered at the anode as PbO_2 (for subsequent thermo-reduction) with high current efficiency. Because of the low current density required to achieve a high anodic current efficiency, this cannot be justified in the light of the cathodic current efficiencies attainable at much higher current densities.

Cathode Deposit

Metallic lead was produced at the cathode and generally the deposit was very spongy and did not adhere well to the cathode. At low current densities (below approximately five amps/sq dm) the deposit became more dendritic than spongy, but was still very loosely attached to the cathode.

Precipitate Formation & Analysis

During both the voltage scans and the electrowinning trials, some precipitate formed during electrowinning. This was most likely due to NH_3 evaporation leading to the lead saturation level dropping below the actual lead concentration. This was evidenced by the precipitate forming faster and in greater quantity in runs that had a high lead concentration as well as where the lead was not being plated out as quickly (i.e., the lead concentration not dropping as quickly). Thus precipitate formation was especially evident in the voltage scans, as the lead concentration was generally much higher over the course of these experiments.

X-ray diffraction patterns for this precipitate were complex and no sure trends could be determined. Atomic absorption analysis showed it to be 75.0% lead, indicating perhaps some mixture of lead oxides, sulphates and basic sulphates. Generally, the cathode deposit was so loosely attached to the cathode, the circulating AAS would wash it off. When the recovered cathode deposit/precipitate mixture was melted, a relatively large quantity of "slag" was produced (being basic lead sulphates). To get a cleaner melt, the precipitate was "washed" out of the cathode deposit (ie., a gravity separation). When "washing" the cathode deposit with water, another precipitate was formed upon dilution of the AAS retained in the cathode deposit. The only patterns discernable in x-ray diffraction analysis of this precipitate were $PbSO_4$ with small amounts of PbO and lead. It is likely that basic lead sulphates were also present. The lead content of this precipitate was 88.5%.

As the formation of these precipitates is undesireable, steps must be taken to reduce or eliminate lead precipitation. For precipitation occurring during electrowinning, control could probably be effected by ensuring that the lead concentration of the AAS going to electrowinning is well below saturation levels. As washing the cathode deposit is necessary to remove the AAS, this can best be accomplished by first washing the deposit with unleaded AAS (to remove the dissolved lead) followed by washing with water to remove the barren AAS.

"Slag" Leaching

The cathode deposits were melted in a small porcelain crucible over a bunsen burner flame, without fluxes. Varying amounts of lead oxides ("slag"), were formed over the molten metal. Any oxides present in the cathode deposit would form PbO; if the dioxide was present, metallic lead may have been consumed in the process (by $Pb + PbO_2 = 2PbO$). If any sulphates were present, they would have reacted with the oxides and/or metallic lead to form Pb_2OSO_4 (i.e., $PbO + PbSO_4 = Pb_2OSO_4$ or $PbO_2 + Pb + 2PbSO_4 = 2Pb_2OSO_4$). Most of the "slag" formed during the melting of the cathode deposits was PbO.

It appears difficult to eliminate oxides from the cathode deposit by washing (and it is anticipated the problem will be exacerbated in the pilot plant by the fine PbO_2 being carried into the electrowinning section from leaching). However, two solutions to handling the slag exist. If pure enough, the PbO may be sold without further processing or it can be returned to the leach section.

To investigate the solubility of the PbO "slag" in AAS, the cathode deposit from the electrowinning experiments was melted and granulated by pouring the molten "slag" and metal into water. This effected a separation of the two phases and it was not difficult to separate the slag granules from the metal.

The slag was ground and leached in two separate experiments. In the first, 32.86 g of slag was agitated in standard AAS for 20 minutes. The final AAS lead concentration was 26 g/l (at this point approximately 30% of the PbO had dissolved).

To see to what extent the slag is soluble in AAS, a series of four leaches was run. 18.77 g of ground "slag" was agitated for five minutes in standard AAS then let settle for ten minutes. The clarified solution was then decanted and fresh AAS added for the next leach. The results were:

Table 5. "Slag" Leaching.

LEACH	Pb CONCENTRATION (g/l)
1	17.6
2	5.3
3	3.3
4	2.1

The total volume from all four batches was 1374 ml analyzing 6.65 g/l lead. Therefore, 9.84 g or 52.4% of the PbO "slag" dissolved.

V. PILOT PLANT DESIGN

A. INITIAL DESIGN

The pilot plant was envisioned to be constructed with two main components; a leaching tank and an electrowinning tank. To keep the design as simple as possible, the pregnant AAS from the leach tank was to overflow directly into the electrowinning tank. The barren solution would then be pumped back to the leach tank. In this circuit an apparatus was also needed for generating NH_4OH to make up for the NH_3 converted to $(NH_4)_2SO_4$ by the process as well as to cover evaporation losses. Some of the calculations made in the design work are shown in Appendix II.

Materials

The material chosen for construction of the main pieces of equipment was lucite (or plexiglas). Lucite is strong, relatively inexpensive, can be readily glued to make strong joints, is easy to machine, will not corrode from the strongly alkaline solutions used and is transparent, which may help in evaluating any problems encountered.

Mild steel was used for the electrodes as no problems were encountered with its use in the preliminary electrowinning trials. Tygon tubing served as piping for the solution as it was readily available and does not corrode.

Leaching Tank

The leach tank served two functions. The first was to separate the three battery components (i.e., plastics, metallic lead and the battery fines) and the second was to dissolve the $PbSO_4$ and PbO contained in the fines. To achieve this, the cross sectional area of the tank increased with height. As the AAS solution flowed upwards through the tank, its velocity would steadily decrease. Thus, the density of the metallics would cause them to sink directly to the bottom of the tank (where they would be removed) and any fines adhering to them would be washed off. Plastics would be entrained in the flow to be carried out the overflow of the leach tank, also having any fines washed off them in the process (this was not evaluated as the plastics were manually separated from the lead bearing materials in the feed used in this study). The fines would be held in suspension to be dissolved at the particular point in the tank where their downward velocity was balanced by the upward velocity of the AAS. The very fine PbO_2 would be washed out of the leach tank and collected in the electrowinning tank with the cathode deposit. Upon melting, the PbO_2 would reduce to PbO to be collected as a separate phase floating on the metallic lead.

The first step in designing the system was to determine the rate at which the battery fines were to be processed and the target for lead concentration in the pregnant AAS. It was felt that a small scale commercial operation may be economical at a processing rate of 1000 batteries per day. With an average of 9.54 kg fines per battery (see "Characterization of Scrap Batteries") and the plant operated 20 hours per day, a fines feed rate of approximately 8 kg per minute would be required. If the bench scale pilot plant was built on a 1/100 scale, the feed rate would be 80 g/min. With a "standard AAS composition" (as used for most of the preliminary experiments), a maximum lead concentration of 50 g/l was expected for the pregnant AAS. Looking at the lead concentration in the electrowinning trials (Chapter IV) where the best current efficiencies were experienced, it appeared conservative to expect 60% extraction during the time the solution was in the electrowinning tank (i.e., the "barren" solution returned to leaching would contain 20 g/l lead). If the fines are successfully pretreated, or if PbO "slag" is fed with the battery fines, we would expect to be dissolving all 80 g of the feed. Therefore, assuming a lead content of 90% in the fines, the required AAS flow rate would be 2.40 l/min.

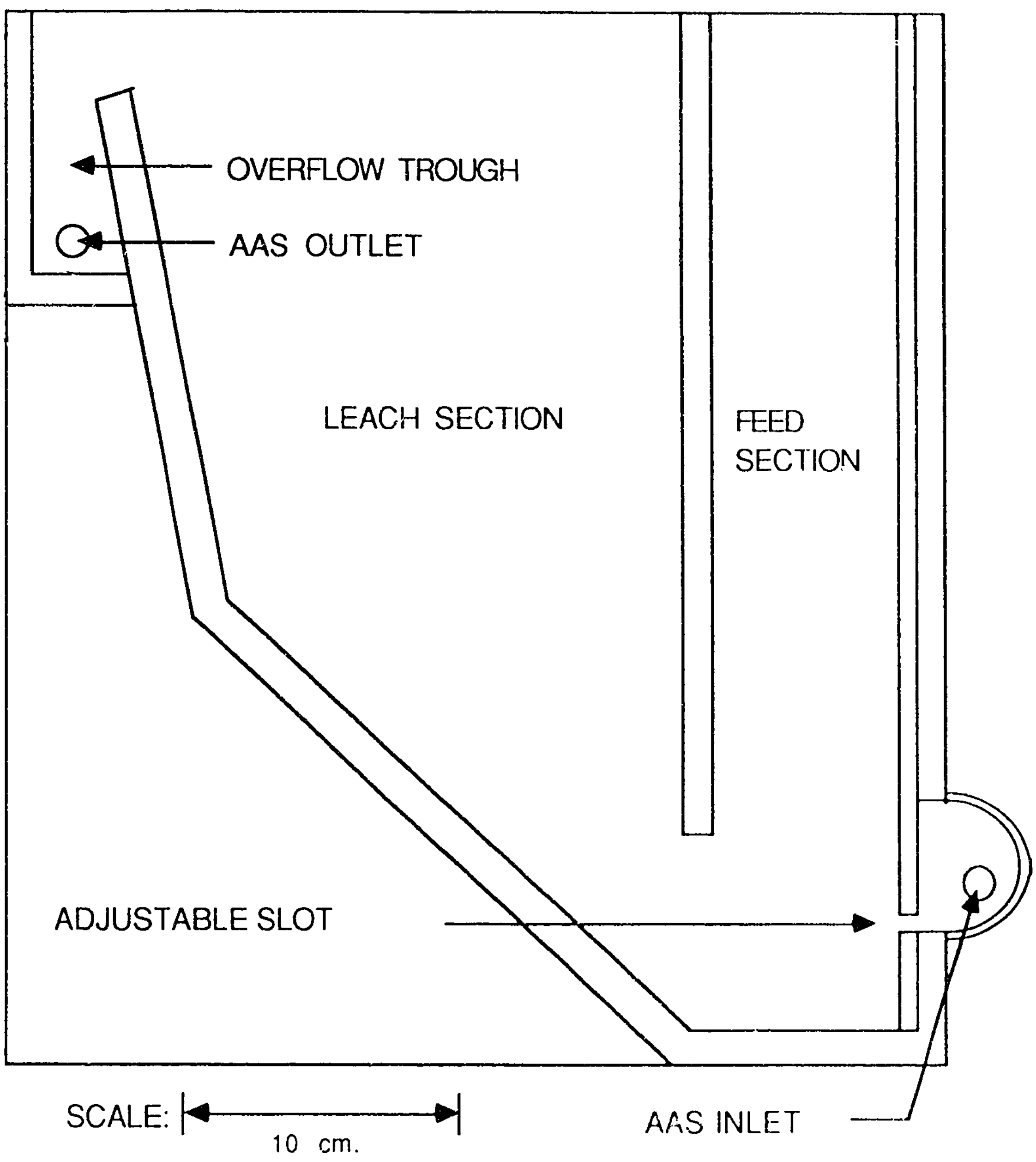
Based on the velocity analysis for the AAS (Appendix II), the velocity of the AAS at the leach tank exit was not to exceed 0.10 cm/s, requiring a cross sectional area at the top of the tank of at least 400 cm^2. With a square cross section for the tank, the dimensions would be approximately 20 cm per side. As the apparatus would have to be operated in a fume hood, this size appeared quite reasonable.

From the "Solubility of Battery Fines in AAS" (Chapter IV), it could be seen that a maximum lead concentration was achieved in approximately 5 to 10 minutes. Therefore, to obtain a minimum five minute retention of the AAS in the leach tank, the tank volume had to be a minimum of 12 litres.

In the actual leach tank design, three more factors were considered. Firstly, the feed had to be introduced into the bottom of the tank where the solution velocity is greatest so that very fine particles would be carried up through the AAS (allowing time for dissolution) preventing them from being carried out of the leach tank as soon as they were introduced. If plastics were in the feed, this would also expose them to the AAS so that fines adhering to them could be dissolved. The second consideration was that the design must prevent turbulence in the upper portions of the tank so that all particles, regardless of their location in the flow regime, would be leached for the same length of time (i.e., again, no short circuiting). Thirdly, the tank cross section must expand very slowly near the outlet so that the flow would be slowed down very gently; if the flow slowed down quickly near the outlet, the chances of creating turbulence would be greatly increased.

The leach tank design (shown in Figure 4) had a passage incorporated behind the leach section for feed introduction. It was intended that feed would drop through this passage where it would hit the horizontal AAS flow from a slot in

FIGURE 4. LEACHING TANK: INITIAL DESIGN



the back of the tank (the slot size was adjustable so that the solution velocity through this slot could be changed). The metallics would fall through the flow while fines would be carried by the flow up into the leaching section. The tank itself had two flow regimes. In the lower section, the vertical flow velocity dropped off quite rapidly (the velocity was relatively high in the lower portion of this section to help keep larger particles in suspension) while in the upper section, the vertical flow velocity was reduced quite slowly. Finally, the AAS overflowed the front of the tank into a collection trough.

The top area of the leach tank was 405.8 cm^2 and the volume of the leach section was approximately 11.8 litres.

Electrowinning Tank

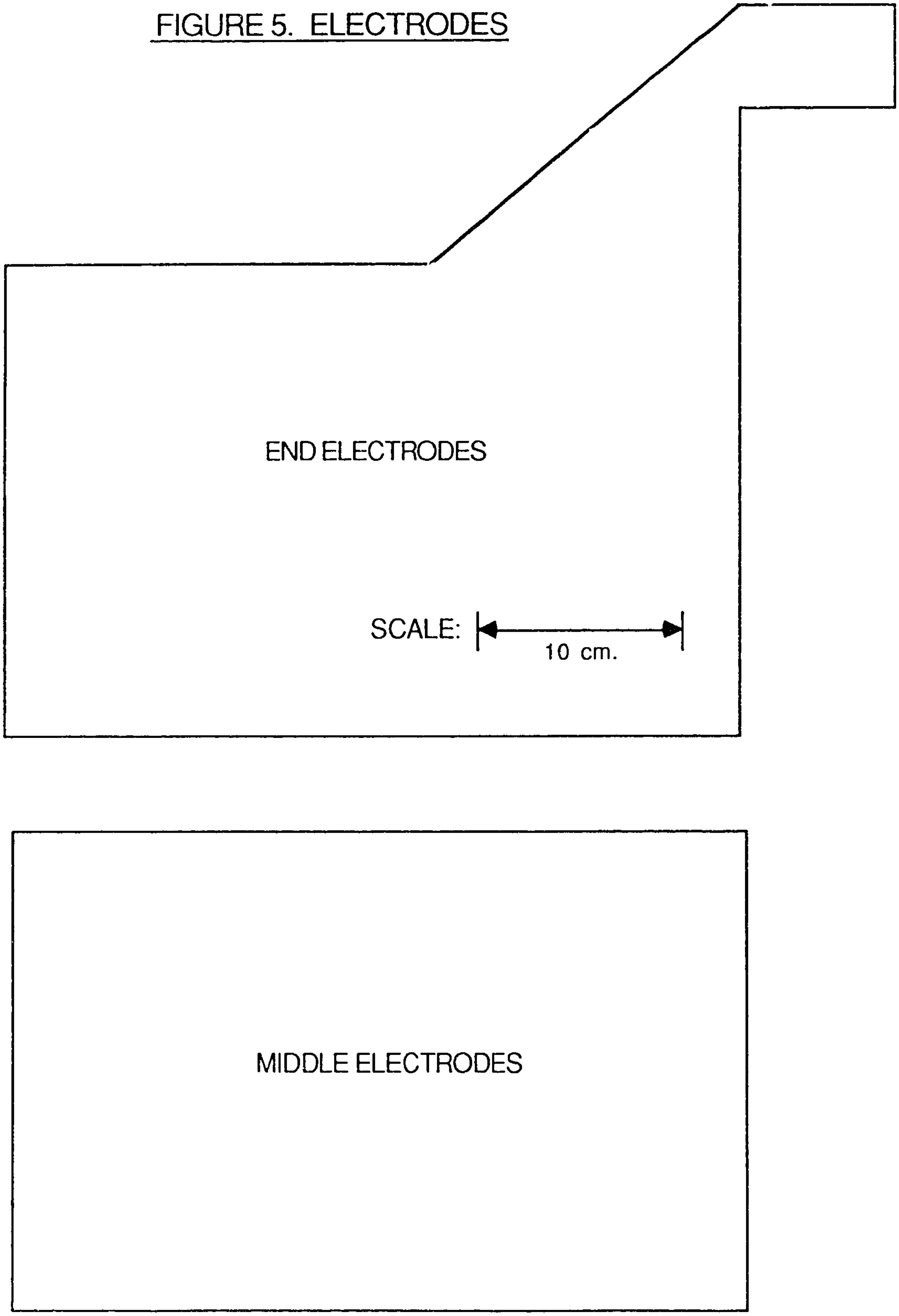
From the "Lead Electrowinning" experiments (Chapter IV), it appeared that the best efficiencies were obtained with current densities in the range of 10 to 15 amps/sq dm. To plate 72 g/min lead at a target 90% current efficiency, a current of approximately 1200 amps was needed. Thus, at 15 amps/sq dm, 80 sq dm of electrode area was required.

As it is difficult to find a power source which will produce 1200 amps at 3 to 5 volts, the electrowinning was broken down into a number of "cells" operating in series. This was accomplished by having two end electrodes connected to the power source with a number of plates suspended in between (but not physically connected). Thus, the end plates operated as an anode and a cathode and for the rest, one side of the plate acted as an anode, the other side as a cathode. The electrowinning was broken down into ten cells, requiring a current of 120 amps at 30 to 50 volts.

To facilitate scraping the cathode deposit and keeping the tank design at reasonable dimensions, rectangular electrodes were used with the long dimension horizontal in the tank. An area of approximately 800 sq cm was needed for each electrode, so using a 2:3 ratio for the dimensions, the electrodes were 23 cm by 35 cm. The two end electrodes had "arms" on them to facilitate the electrical connections. The two end electrodes and nine middle electrodes were cut from 0.32 cm mild steel sheet (Figure 5).

The tank itself was constructed from 1.3 cm lucite with slots machined in the sides to hold the electrodes 13.5 cm above the tank bottom (to allow for accumulation of the cathode deposit). Fifty one slots were machined on 1 cm centres to allow for spacing the electrodes up to 5 cm apart. The total depth of the tank was 43 cm so the electrodes could be completely immersed in the AAS solution. The pregnant AAS solution overflowed into the top of the tank in front of the electrodes. At the opposite end of the tank, an exit nipple was put behind a baffle, 12 cm off the floor; the baffle was to prevent falling cathode deposit from entering the return line and the height of the nipple prevented cathode deposit on the tank floor from entering the return line. An overflow tube was also installed to keep

FIGURE 5. ELECTRODES



the fluid level three cm below the top of the tank. The electrowinning tank is shown in Figure 6.

Auxillary Equipment

Ammonia Contactor

It was not known how readily anhydrous NH_3 would dissolve in strong NH_4OH, so a contactor was constructed. A 60 cm length of 15 cm diameter PVC pipe was filled with Raschig rings and caps were cemented on both ends. An outlet nipple was installed on the side at the bottom and an inlet nipple put on top at the center of the cap. The inlet for the NH_3 was put on the bottom. Thus, NH_3 gas would enter the contactor at the bottom and the AAS would flow down through the Raschig rings providing a substantial surface area of AAS for NH_3 absorption (Figure 7).

Pump

The pump used was a *Flotec* "drill pump" model F2P4-1062. The pump speed was controlled with a *Superior Electric* variable autotransformer (type 116).

Power Source

Electrical power for the electrowinning was provided by a *Hobart* R-600-S welder which produced rectified (3 phase) direct current.

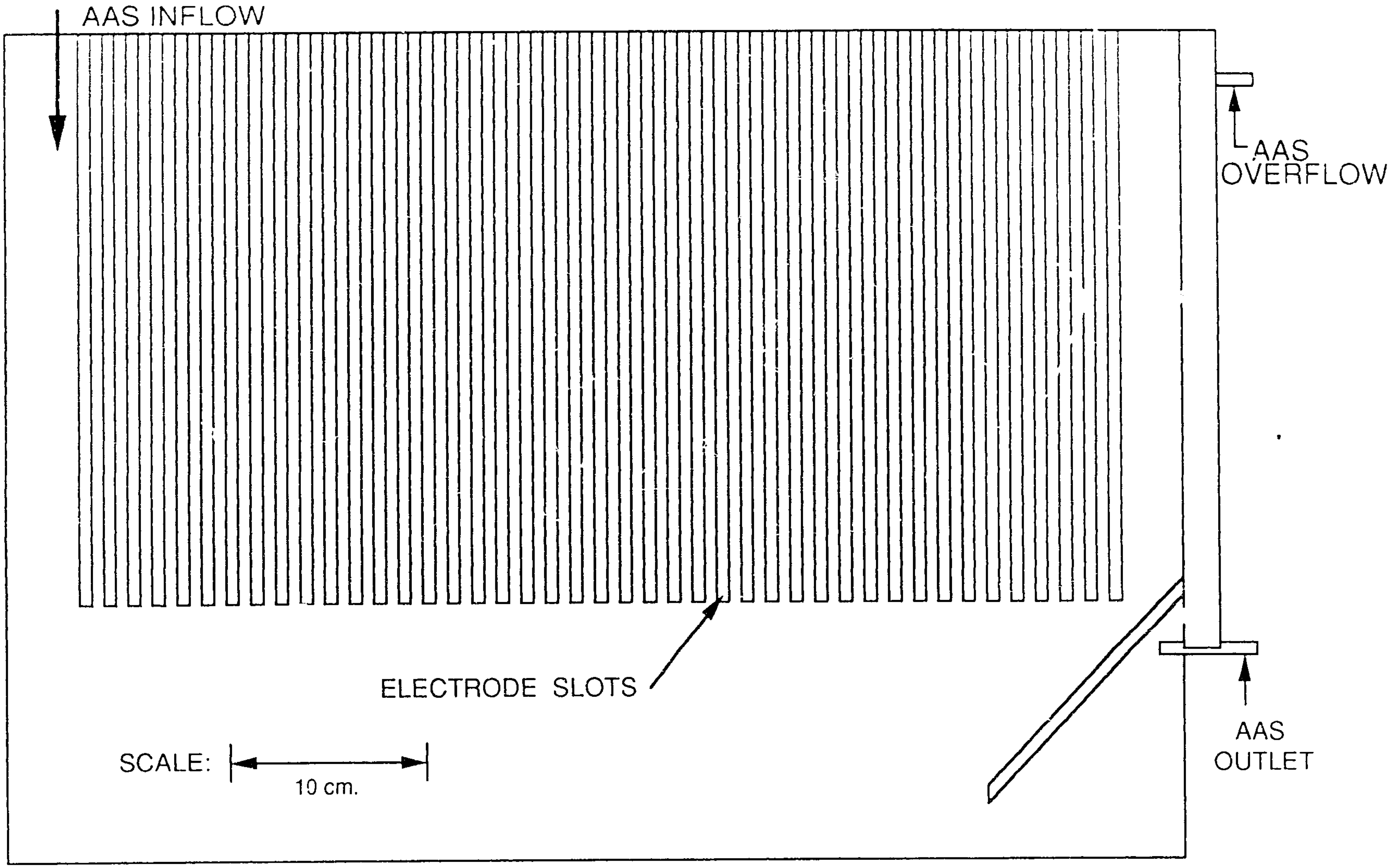
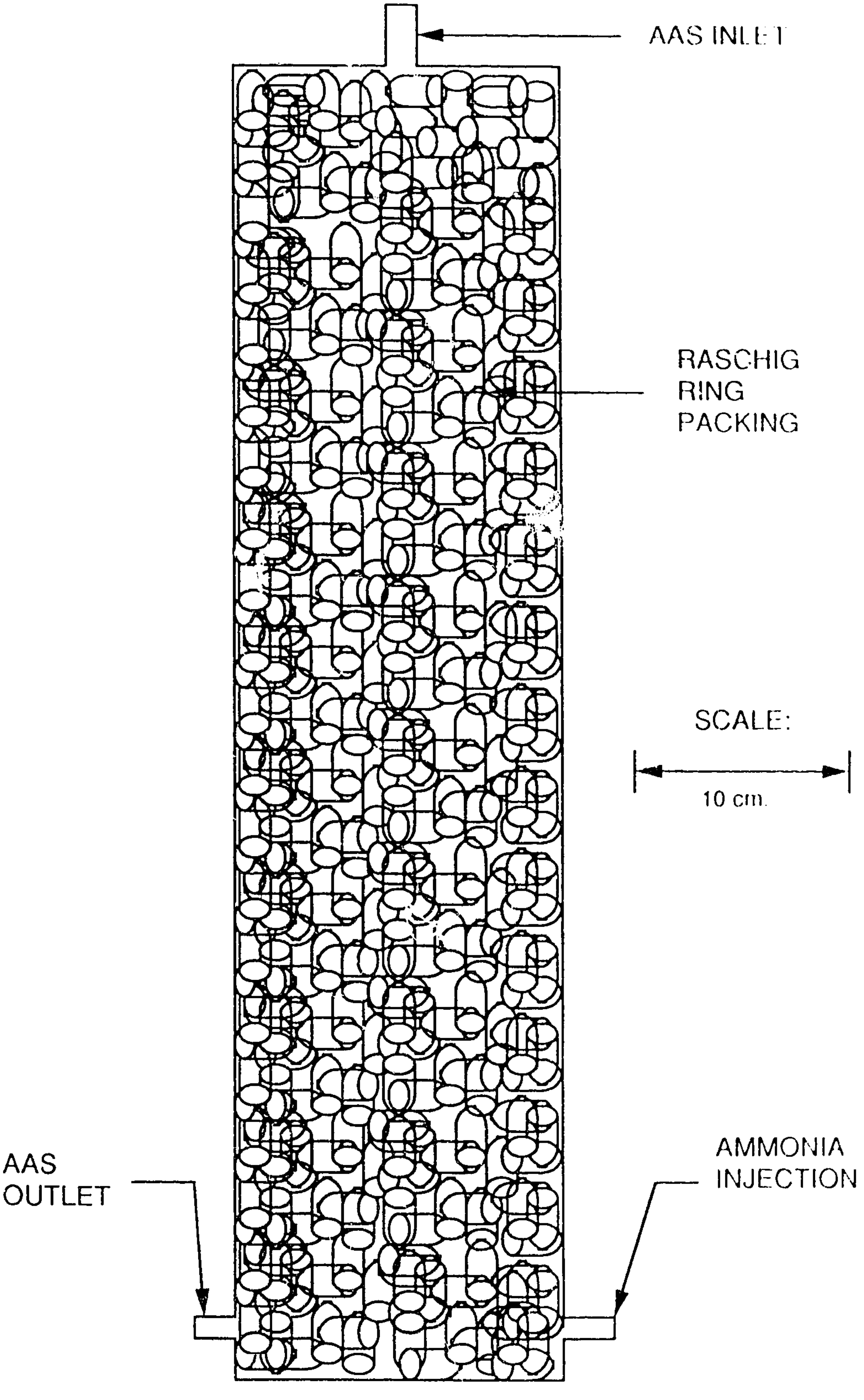


FIGURE 6. ELECTROWINNING TANK

FIGURE 7. AMMONIA CONTACTOR



B. TESTING AND REDESIGN

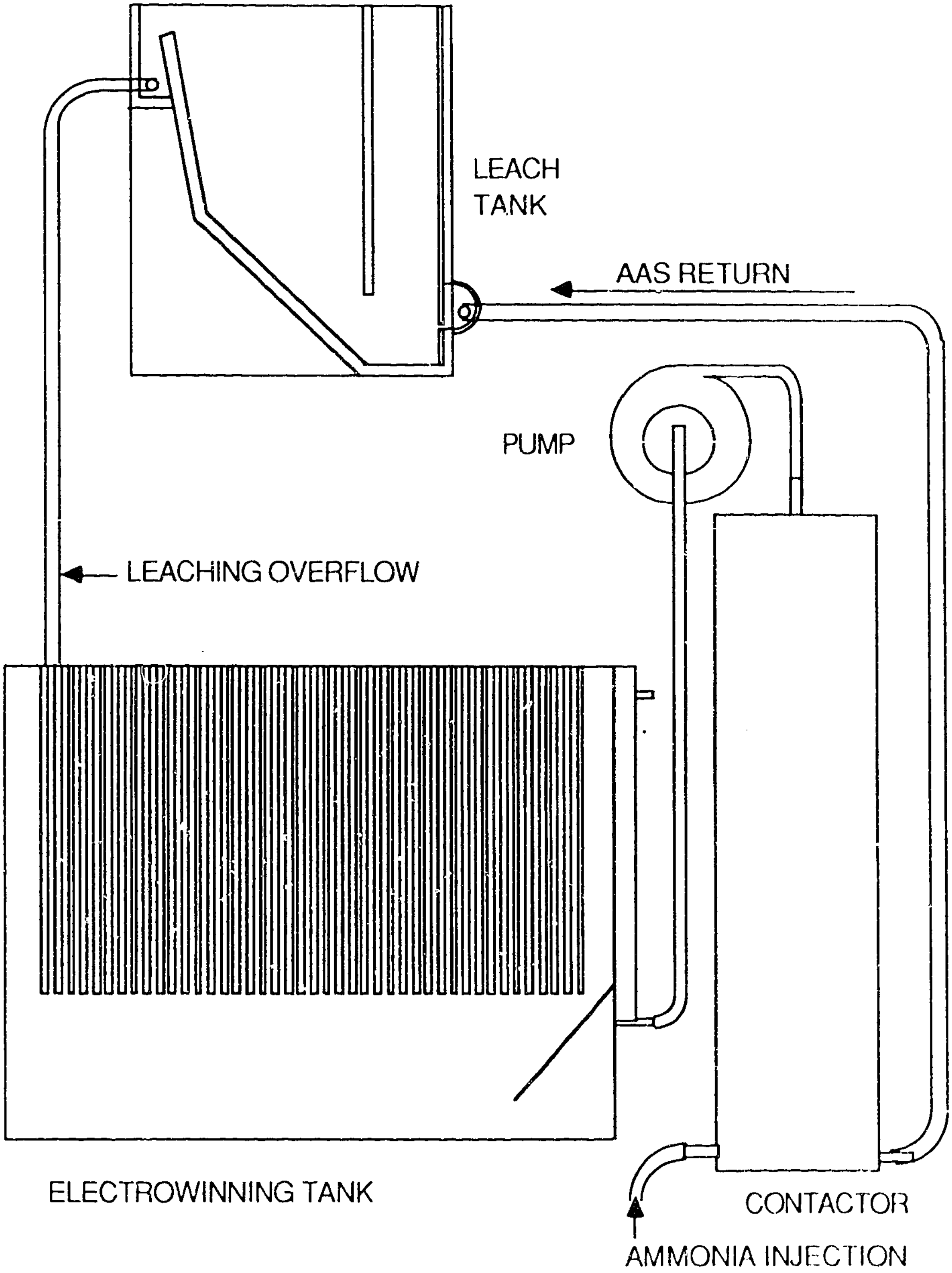
Trials Using Original Design

The pilot plant was initially set up as shown in Figure 8.

First Trial Run

The purpose of this run was to produce an AAS solution for subsequent tests; no battery material was leached. NH_3 was injected into the NH_3 contactor from a 7 kg NH_3 cylinder. For the first 60 minutes the NH_3 was set at a static pressure of 41.2 kPa (6 psig) and for the second 60 minutes the NH_3 was set at a static pressure of 82.8 kPa (12 psig). In both cases the pressure while flowing was approximately 13.8 kPa (2 psig). Two problems occurred with the NH_3 contactor. First, the NH_3 reacted inside the feed line to the contactor, not inside the contactor itself. Evidently, there is a critical pressure required for the reaction to begin and it is only a few centimeters of water. This pressure was obtained by pushing the water in the feed line up into the contactor. When the critical pressure was reached the reaction occurred violently, drawing the water back into the feed line. The reaction would stop and the NH_3 gas would then again start pushing the water back up the feed line. The second problem encountered was frosting of the NH_3 bottle. Gas was taken from the cylinder at a relatively high rate. The evaporation of the liquid NH_3 inside the cylinder lowered the temperature of the liquid

FIGURE 8. PILOT PLANT: INITIAL SETUP



NH_3 to its boiling point, lowering the cylinder pressure and greatly reducing the NH_3 gas flow. Frost on the outside of the cylinder served to insulate it, further slowing the heat flow from the surrounding air into the cylinder. Thus, the flow obtained was inadequate to give acceptable NH_3 levels in the AAS as well as making it impossible to maintain a constant NH_3 feed rate.

In spite of the NH_3 problems, a second run was attempted to evaluate the rest of the apparatus under full operating conditions (i.e., with battery fines feeding and electrowinning).

Second Trial Run

In this run, battery fines were fed dry into the leaching tank at 80 grams per minute (i.e., 400 g batches were fed over five minutes). Attempts to slurry the battery fines with AAS to eliminate air bubbles from the feed (surface tension would then cause some of the feed to float) were unsuccessful as the battery fines quickly formed a cemented mass in the bottom of the beaker (this mass was hard enough that it had to be chipped out of the beaker).

The battery fines feeding was stopped after 45 minutes as the material, upon being introduced into the leach tank, immediately sank to the bottom and stayed there. Attempts to get the material into suspension were unsuccessful. These included manual stirring of the material, increasing the AAS flow rate and narrowing the AAS feed slot to increase the solution velocity at the bottom of the tank. Lead analysis of the AAS showed that (expectedly) the lead compounds were not dissolving in the AAS when they were sitting on the bottom of the leach tank.

The frosting problem with the NH_3 cylinder again resulted in inadequate NH_3 flow rates, 30 minutes into the run.

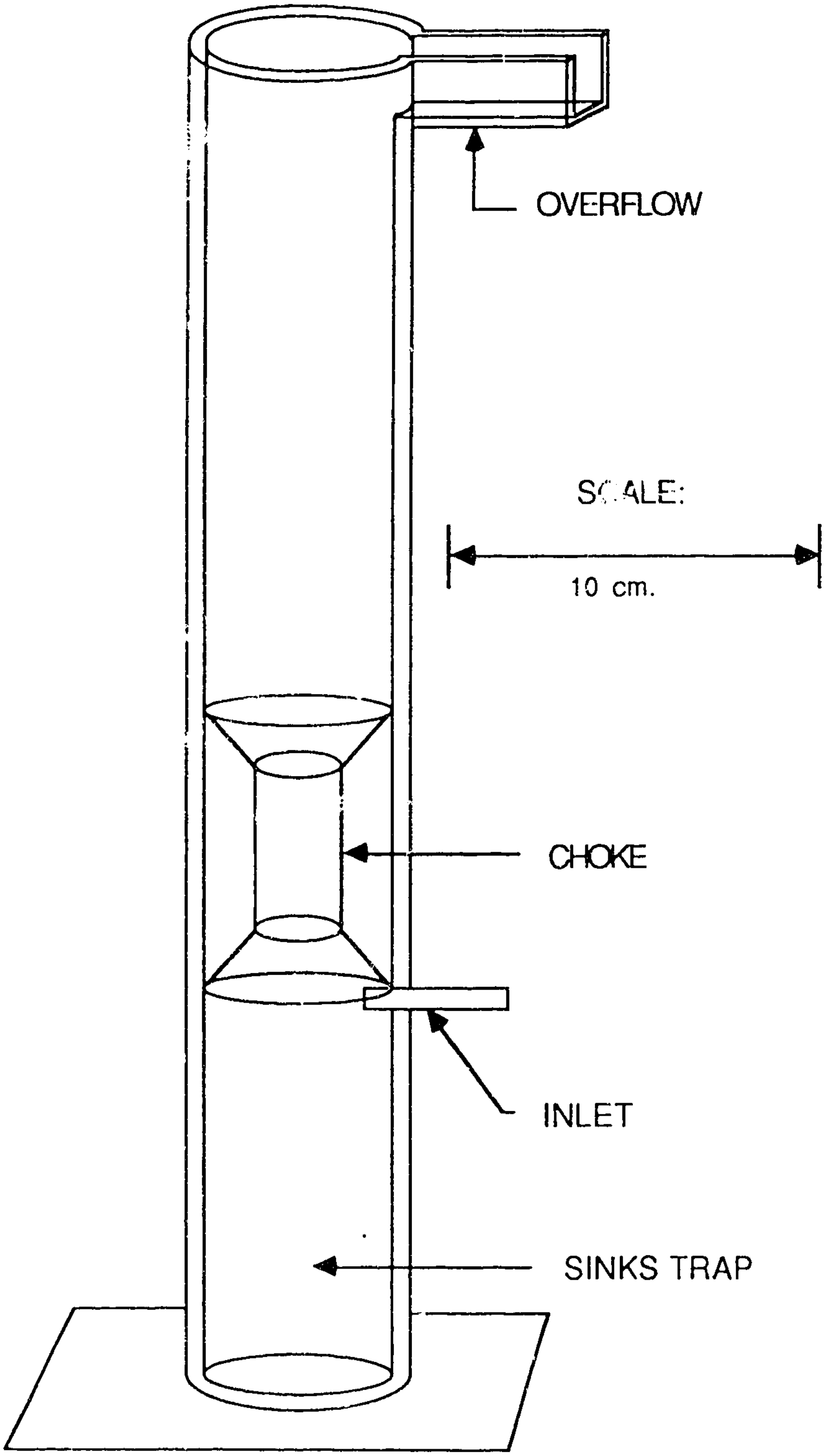
Leach Section Redesign

From the first two trial runs, it became evident that the initial design of the leaching system was inadequate in that the velocity and flow pattern did not keep the battery fines in suspension and were not effectively separating the battery components. Also, measures were needed to ensure a constant NH_3 flow to the leach system.

Separation Experiments

To determine the AAS flow velocity needed to ensure a good separation of the battery fines (and hold the pastes in suspension), a small leach column was constructed from a 5 cm (I.D.) lucite cylinder (Figure 9). A 2.5 cm choke was installed in the middle of the column and water was pumped into the bottom of the column so that it flowed upwards through the choke and up through the column to overflow into a settling tank. The flow rate was set by measuring the overflow for a fixed time period, then 200 g of battery fines were introduced into the column. The system was run approximately 10 minutes, then the separated fractions were collected, dried and weighed. Because the test column was cylindrical, all the material either sank or was washed out

FIGURE 9. SEPARATION TEST COLUMN



of the cylinder. Figure 10 shows the separation at different flow rates.

The final design of the leach column is shown in Figure 11. It consisted of an inverted cone made from a 1 meter length of 20 cm diameter PVC pipe. There was a 2.5 cm choke at the bottom of the inverted cone connecting the cone to a trap made of 15 cm diameter PVC pipe with a threaded cap on the bottom. This cap allowed for cleaning out the heavy material that sank through the choke. It was into this trap that the NH_3 was injected and also where the AAS was returned to the leaching column from electrowinning. An overflow pipe was attached to the top of the cone to direct the overflow into the electrowinning tank. A feed tube extended into the cone to introduce the feed material approximately 10 cm above the choke.

Third Trial Run

The third trial run used the apparatus shown in Figure 12. The new leach column was set up to overflow directly into the electrowinning tank, then the AAS was pumped from the electrowinning tank back into the bottom of the leach column. A 45 kg cylinder of NH_3 was used to provide a steady NH_3 flow rate (by providing more area for heat transfer and a larger reservoir of liquid NH_3 from which to evaporate gas). The NH_3 was injected into the trap at the bottom of the leach column and a flow meter was installed in the NH_3 line to give a more accurate measure of the NH_3 feed rate.

FIGURE 10. SEPARATION TEST COLUMN RESULTS

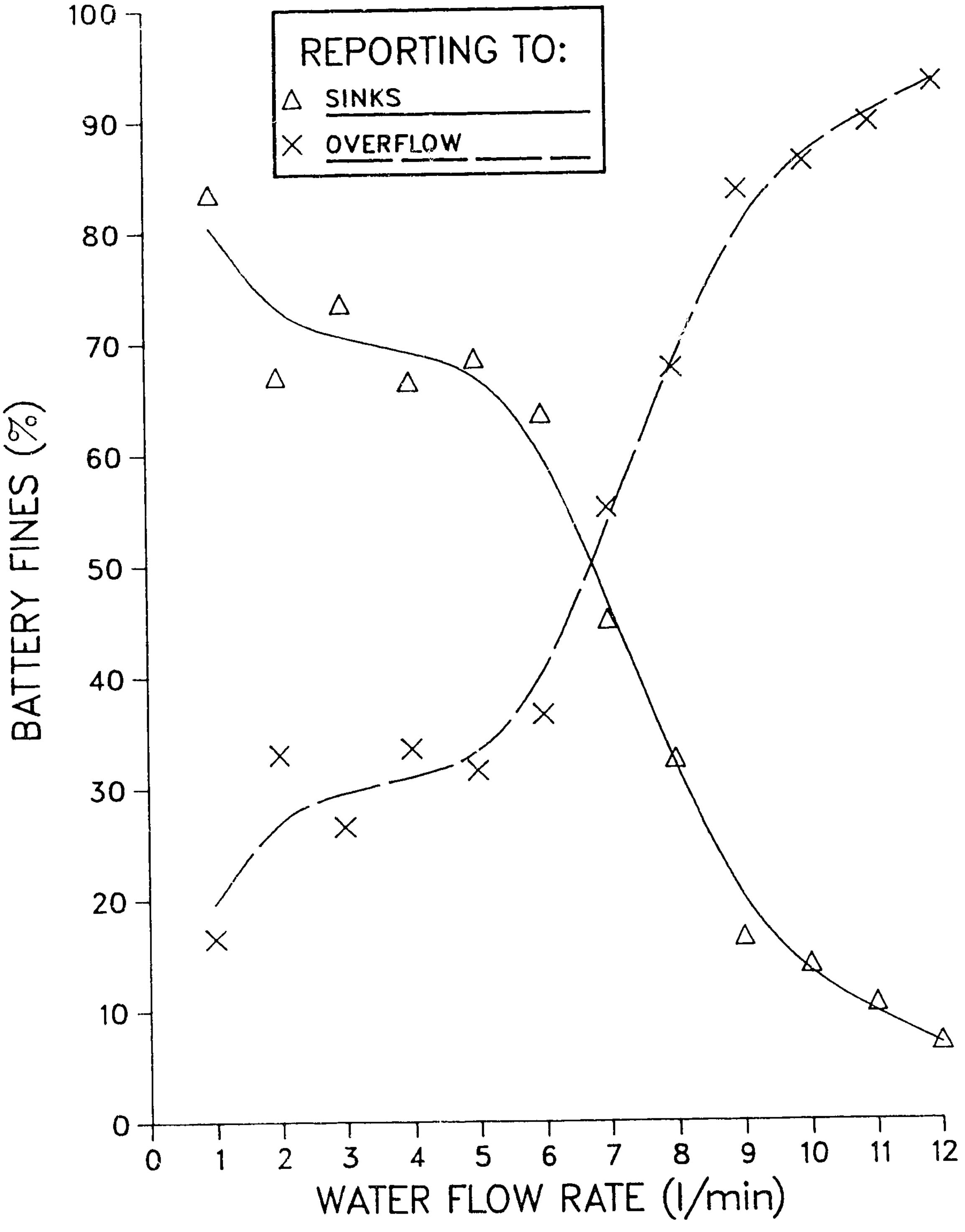


FIGURE 11. LEACH COLUMN: FINAL DESIGN

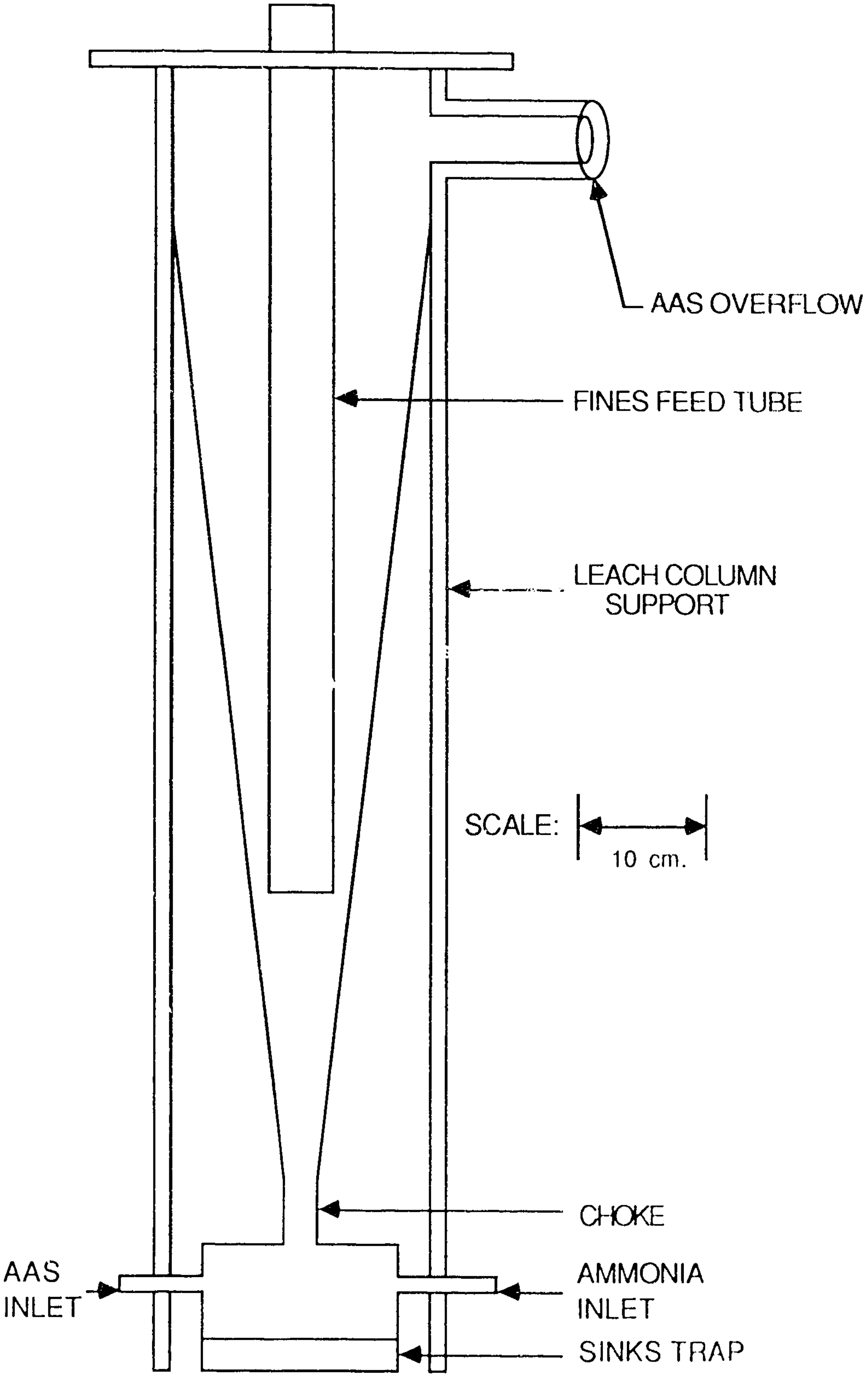
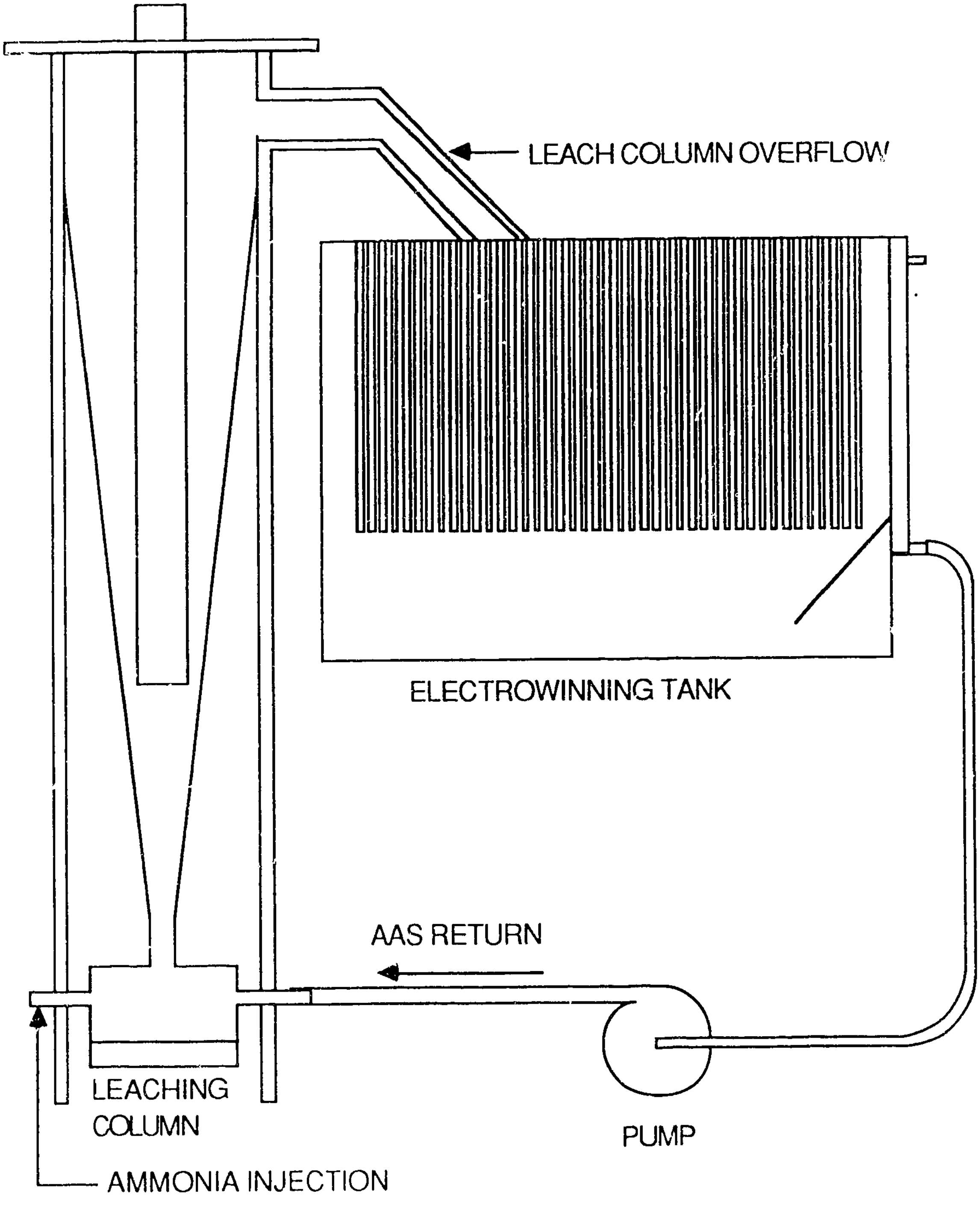


FIGURE 12. PILOT PLANT: TRIAL RUNS



The run consisted of injecting NH_3 into the circulating AAS for two hours to build up the NH_3 concentration. The battery fines were then fed for one hour to allow the lead concentration to build up before the power was turned on to the electrowinning section. Battery fines were fed at 60 g/min by slurrying 600 g with water and feeding over a ten minute period. This eliminated the feeding problems previously encountered. The electrowinning current was held at 60 amps with 12 volts. The fines feeding was stopped two hours after the power had been turned on to electrowinning, but AAS circulation to electrowinning was continued for a further 1/2 hour to finish leaching the fines in the column and to allow the electrowinning to reduce the AAS lead concentration (to reduce the probability of lead precipitation during storage).

The system operated quite well, except the NH_3 flow dropped off after three hours due to the 45 kg cylinder frosting. Also, NH_3 leaks at the flow meter connections proved impossible to stop.

Fourth Trial Run

The apparatus for this run was the same as the third trial run, except for changes to the NH_3 feed. The NH_3 flow meter was eliminated and liquid NH_3 was injected into the leach column by inverting the 45 kg cylinder and replacing the tygon line with a stainless steel *swagelok* line. The flow rate was adjusted by a needle valve installed in the NH_3 feed line right at the column.

This run went well and the system operated as anticipated. The NH_3 valve and line right at the leach column frosted up, but it did not affect the NH_3 flow. It was found that the NH_3 feed rate can be estimated by the "rumbling" effect produced in the column. (When the liquid NH_3 goes through the valve it immediately evaporates, then the bubble comes into contact with the AAS and dissolves in the water, collapsing the bubble. It is the violent collapsing of these bubbles which produces a rumbling sound inside the leach column.)

The only serious problem encountered with this run was in melting the cathode deposit. The deposit converted to a lead oxide/sulphate "slag" upon melting and no metallic lead was recovered.

Settling Tank Installation

Inspection of the cathode deposit revealed that a substantial proportion of the battery fines was being washed out of the leach column and was mixing with the cathode deposit in the electrowinning tank (these fines consisted of both PbO_2 and $PbSO_4$). It was anticipated that, due to its fineness, only PbO_2 would be washed into the electrowinning tank. This could be tolerated when melting because it would produce a PbO phase in addition to the metallic lead. The PbO could then be recovered as a final product or returned to the leaching circuit. The amount of PbO_2 and $PbSO_4$ being carried over, however, made this approach impossible.

In an attempt to eliminate this contamination, a settling tank was constructed from the bottom of a polypropylene 45 gallon drum. The design followed that of a conventional thickener (Figure 13); the solution enters the tank at the center and a trough around the circumference collects the clarified AAS as it overflows the periphery of the tank. The trough leads to a spout which discharges the clarified AAS into the electrowinning tank.

Fifth Trial Run

The apparatus was the same as for trial run four, except for the settling tank installed between the leach column and the electrowinning tank (Figure 14).

For this run the AAS flow rate was set at 7.7 l/min and battery fines were fed at 30 g/min. Battery fines were fed for 2 hours. The power was turned on 30 minutes after fines feeding was begun and continued for 60 minutes after fines feeding was stopped.

The pilot plant worked very well. No feeding or NH_3 problems were encountered and the cathode deposit melted easily into metallic lead. Thus, the system as shown in Figure 14 was the pilot plant as used for the operating runs.

FIGURE 13. SETTLING TANK

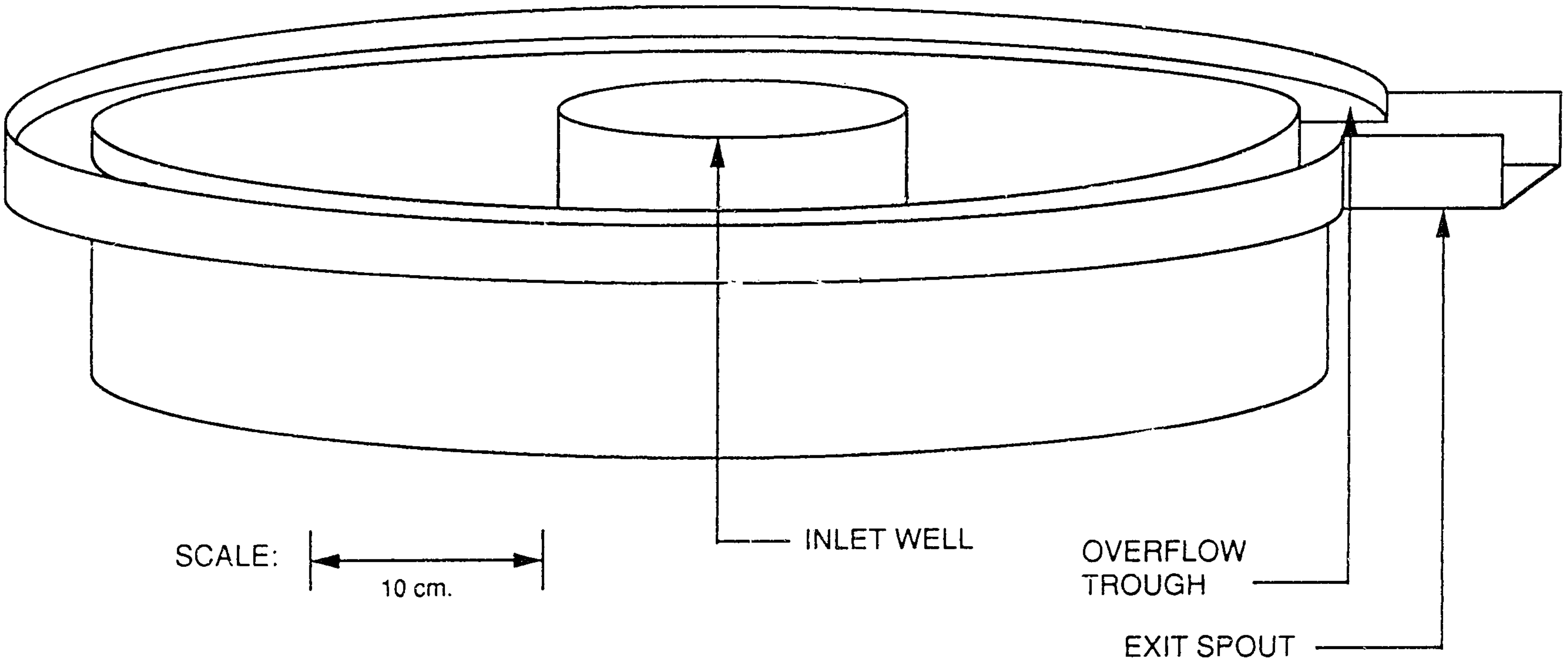
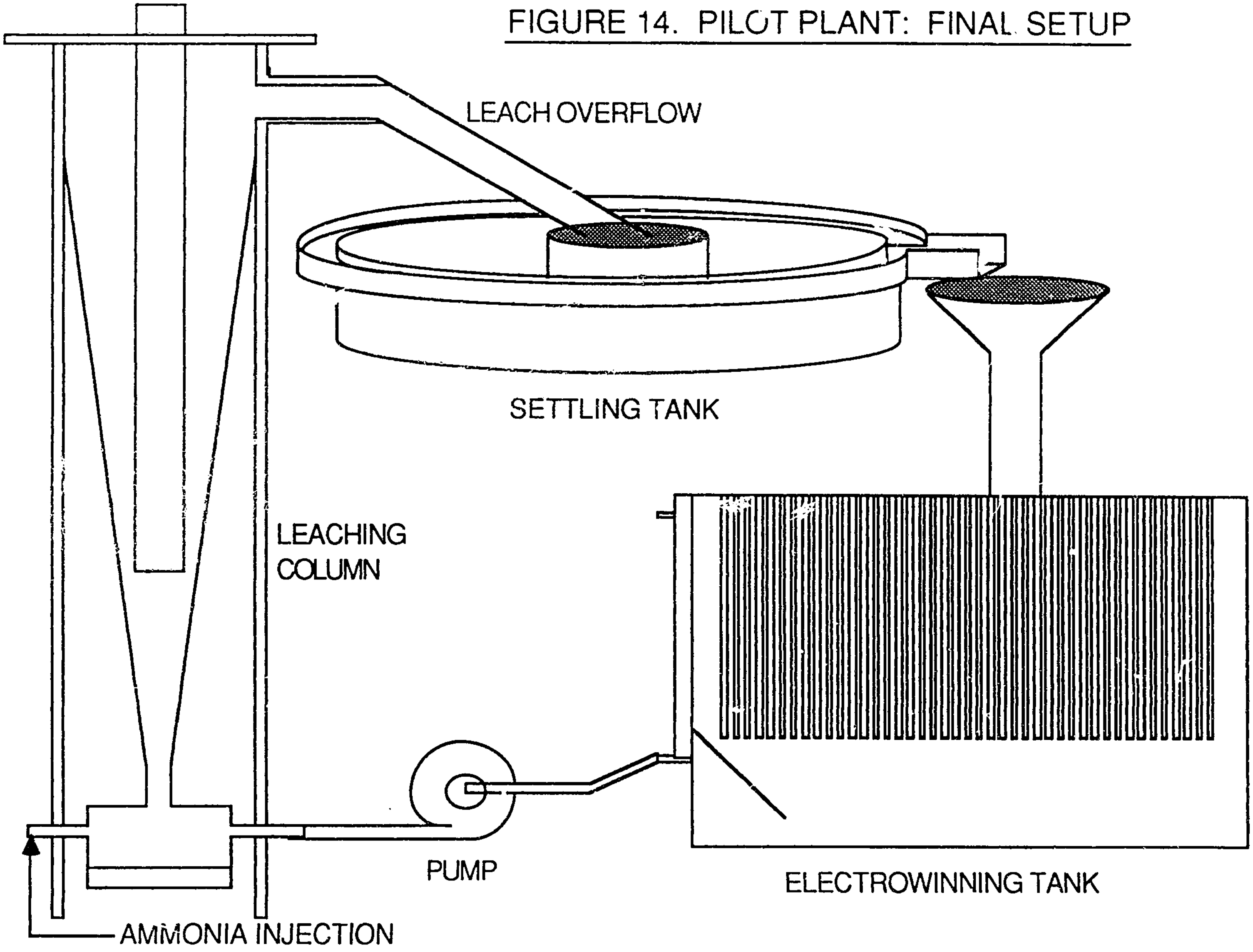


FIGURE 14. PILOT PLANT: FINAL SETUP



VI. OPERATING RUNS

Method of Operation and Monitoring

The pilot plant was operated in "runs" which were generally 2 hours long. Before each run was started the pump speed was set to achieve the desired AAS flow rate, measured by diverting the flow from the settling tank into a 1 litre beaker for a measured length of time, then measuring the volume of AAS collected with a 1 litre graduated cylinder. To start each run, the power was turned on to the electrowinning and set at the desired level at the same time as feeding of battery fines was begun. Generally, 2 hours provided enough time that the plant would reach a "steady state". As feed was needed, 10 minutes worth of dried, ground battery fines were weighed out into a beaker. The feed was then slurried with water and slowly fed into the leach system over 10 minutes. Although this did not result in perfectly continuous feeding, we did know that the correct amount of feed was introduced over each 10 minute period.

Throughout the run the cathode deposit was scraped as often as required to prevent short circuiting. The deposit was removed from the electrowinning tank as much as possible and at the end of each run the cathodes were thoroughly scraped and the loose deposit collected from the bottom of the electrowinning tank.

Every 15 minutes during the run a sample of the AAS solution was taken from the electrowinning tank and sealed in a plastic bottle. These samples were then analyzed by atomic absorption spectrophotometry for the lead content. The NH_3 content was determined by titration with a standardized 3M H_2SO_4 solution using methyl red as an indicator. The $(NH_4)_2SO_4$ content was determined by evaporation. It was assumed that, upon evaporation of the NH_3, the lead precipitated out as Pb_2OSO_4 and that only the Pb_2OSO_4 and $(NH_4)_2SO_4$ remained after drying. The weight of Pb_2OSO_4 was calculated from the lead concentration analysis and subtracted from the total weight of solids left by evaporation to arrive at the $(NH_4)_2SO_4$ content.

At each 15 minute interval, in addition to taking the AAS sample, the voltage and current for the electrowinning were recorded. The voltage was measured directly (across the two end electrodes) and the current was determined with a millivolt meter and a 400 amp shunt installed in series with the electrodes.

The ammonia feed rate was averaged over the entire run as adjustments generally had to be made during the run to compensate for changes in the NH_3 feed rate, due to temperature changes in the valve. The feed rate was determined by weighing the NH_3 bottle before and after the run.

The weight of the cathode deposit was recorded after melting. This gave a conservative value, as some of the deposit would inevitably be oxidized during melting. To simply wash, dry and weigh the cathode deposit would result in a higher weight than what was actually electrowon, as during washing some of the dissolved lead in the AAS that was entrained in the cathode deposit would precipitate as Pb_2OSO_4. It was very difficult to wash the Pb_2OSO_4 out of the deposit without losing a portion of the cathode deposit. The weight of separated metallics (sinks) was recorded both after the sinks were dried and after melting. All melting was done using a #50 silicon carbide crucible in a propane fired furnace. The melting was accomplished in one half hour at 1000°C.

Between runs, the AAS solution was pumped into sealed plastic pails or a plastic drum to prevent NH_3 losses during storage. The same AAS solution was used for all the operating runs.

A. OPERATING RUNS

As outlined in the previous section, runs generally lasted 2 hours. A series of runs was used to evaluate and optimize each variable in the process, these being:

1) Electrowinning voltage and current.

2) The rate at which battery fines are fed into the system.

3) The NH_3 feed rate.

4) The AAS flow rate.

5) The effects of various organic additives on electrowinning and leaching.

6) Treatment of battery fines and settling tank slimes with H_2SO_4.

7) Electrode spacing.

8) Electrowinning voltage and current (tested on a narrower scale than the first runs).

9) A final run was performed under the optimum conditions determined by the previous runs, using unseparated battery material (i.e., whole battery plates were ground; none of the metallics were removed manually).

The data collected during each run were total NH_3 consumption, AAS flow rate, battery fines feed rate, electrode spacing, cathode deposit weight after melting and leach column sinks weight after drying and after melting. Also, the AAS lead and NH_3 concentrations and the electrowinning voltage and current were measured every fifteen minutes during the runs. The $(NH_4)_2SO_4$ content was analyzed only at the beginning and end of each run.

Using these data, two sets of calculations were performed. The first included current density, current efficiency, specific energy consumption (kWh/kg Pb produced), NH_3 consumption (kg NH_3/kg Pb produced) and the steady state lead concentration was estimated. The second set of calculations was mainly a material balance to show where lead was recovered in the system. The efficiency with which leaching was accomplished was determined as the amount of lead actually dissolved (the net amount of lead going into solution plus the amount of lead recovered as cathode deposit both expressed as an equivalent amount of $PbSO_4$ that would have to dissolve to yield this amount of lead) divided by the amount of material available to be dissolved (the total amount of battery fines fed less the weight of the leaching column sinks). The final calculation was the efficiency with which the column sinks were cleaned (the weight of metal after melting divided by the total weight of dried sinks).

Run 1: Electrowinning Voltage and Current

This set of seven individual runs explored the current efficiency and power consumption experienced with the system at electrowinning currents of 4, 13, 26, 50, 85, 120 and 170 amps (or 0.5, 1.6, 3.3, 6.1, 10.4, 15.1 and 20.6 amps/sq dm, respectively). Throughout these runs, the AAS flow rate was set at 9 l/min, the battery fines were fed at 50 g/min, ten electrodes were used (giving nine cathodes and nine anodes) spaced 3 cm apart on center and agitation in the electrowinning tank was provided by three overhead stirrers.

For the first run of the series, the fines feeding was begun 105 min. before the power was turned on to electrowinning, in order to build up the lead concentration in the AAS. For each pair of runs after, the first had the power turned on after 15 minutes of fines feeding, the second of each pair had the power and feeding started simultaneously. For all runs, the electrowinning was carried on for 2 hours.

The NH_3 feed rate for the first set of runs was not determined although it can, to some extent, be inferred from the NH_3 levels in the AAS. The column sinks for all seven runs were not weighed individually.

The current efficiency (Figure 15) was highest at the 50 amp setting (34.5%) and from there fell off with higher amperage. Unexpectedly, the current efficiency was low for 27 amps and lower.

Generally, higher current densities resulted in a lower steady state lead concentration (Figure 16). This in turn allowed for greater dissolution of the feed. Thus, higher current densities resulted in higher leach efficiencies (Figure 17). The first run (0.5 amps/sq dm) is exceptional because it was the initial run, starting with a low lead concentration. The feed that was dissolved to bring up the AAS lead concentration results in the misleadingly high leach efficiency.

As increased recovery is important, but not at the expense of current efficiency, subsequent runs were operated at 50 amps (6.1 amps/sq dm). In addition to the highest current efficiency, this amperage had the second lowest energy consumption. Also, this amperage can plate 32 grams of lead per minute (with 10 cathodes and 100% current efficiency) which will balance the lead dissolving at over 90% leaching efficiency with a 50 g/min fines feed rate. The results for Run 1 are shown in Appendix III.

FIGURE 15. RUN 1: CURRENT EFFICIENCY

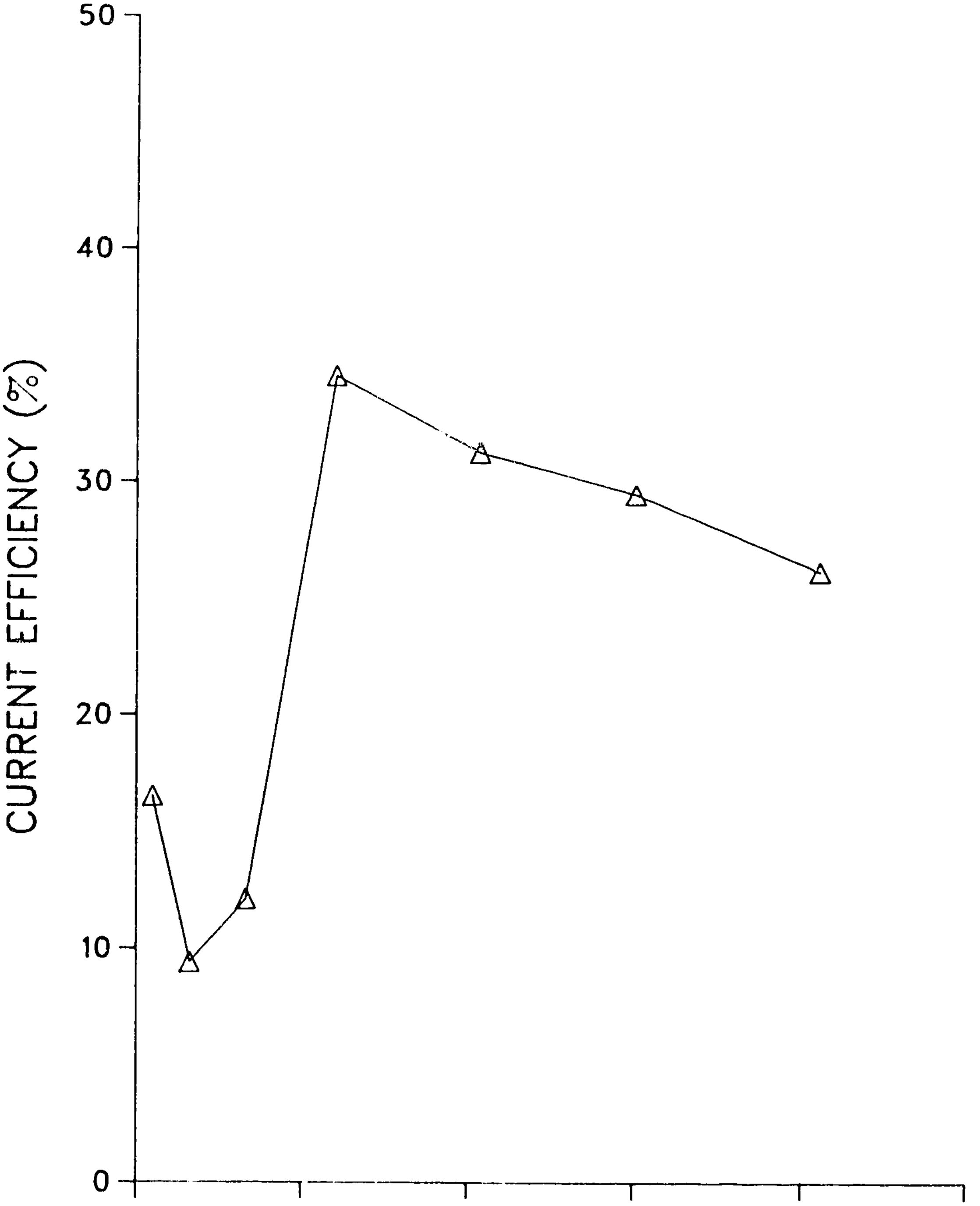


FIGURE 16. RUN 1: STEADY STATE LEAD CONCENTRATION

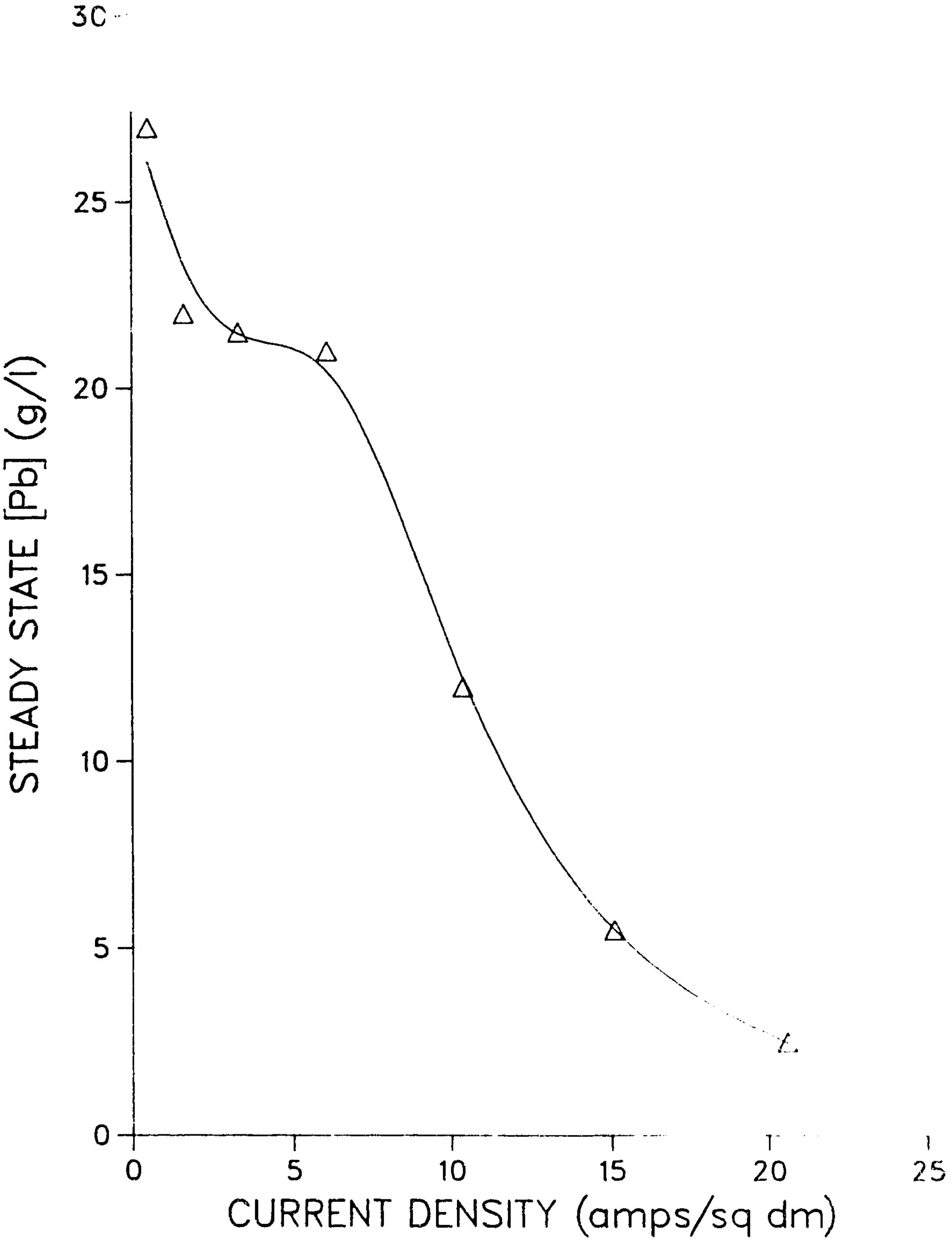
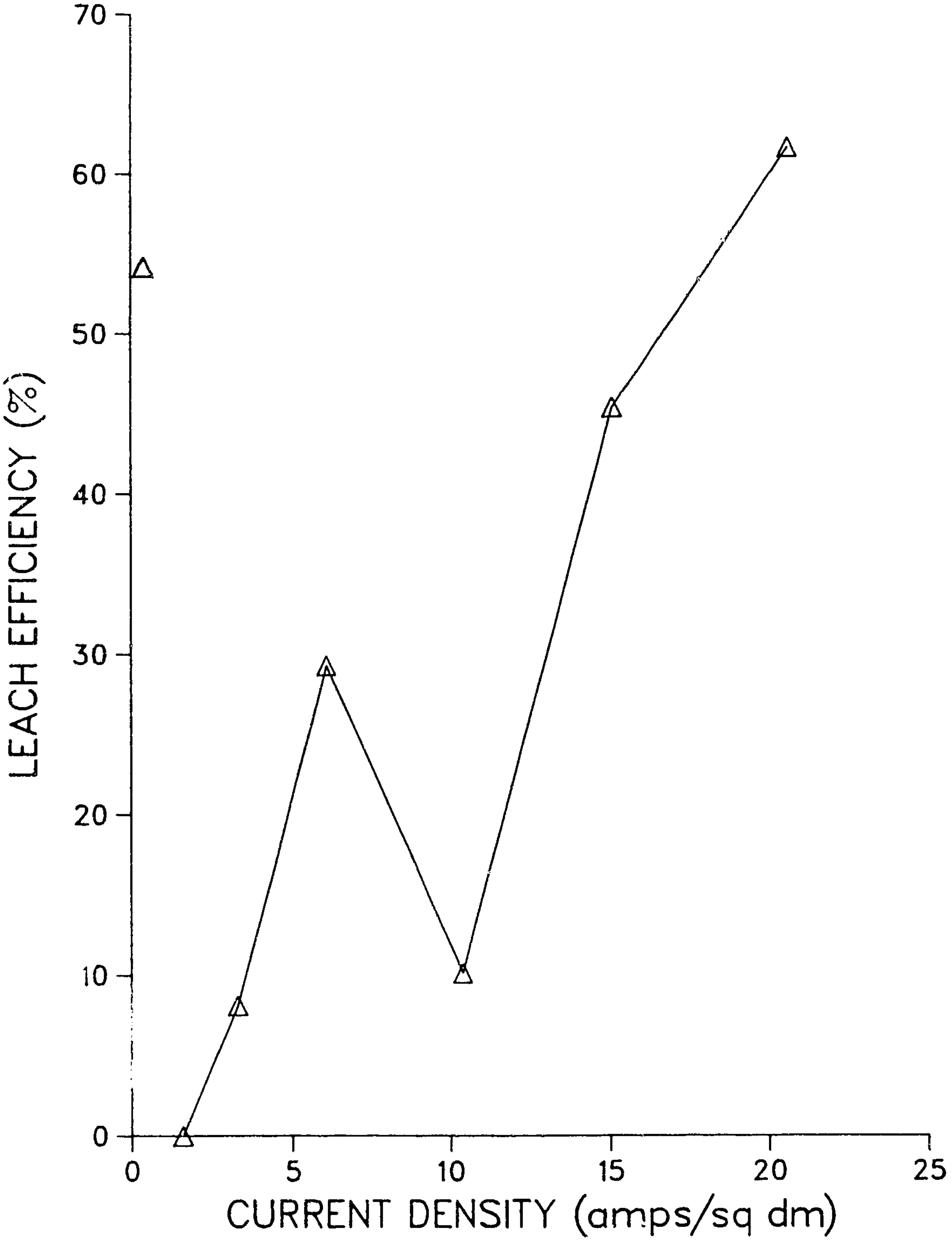


FIGURE 17. RUN 1: LEACH EFFICIENCY



Run 2: Battery Fines Feed Rate

The second set of runs explored the effect of the battery fines feed rate on the performance of the system. The feed rates used were 10, 25, 50, 75, 100 and 150 g/min. These were performed using exactly the same apparatus as for the first set of runs.

For each run, the fines feeding, electrowinning power and NH_3 feed were all started simultaneously. The amperage was maintained at 50 amps, the AAS flow rate was set at 9 l/min and the NH_3 feed rate (which was only measured over the final run) was approximately 60 g/min.

The cathode deposit and sinks were weighed after each run. The data for these runs are shown in Appendix III.

It was expected that higher feed rates would provide more $PbSO_4$ exposure to the AAS, resulting in higher lead concentrations (Figure 18) and correspondingly higher current efficiencies (Figure 19). This is borne out by the data. Also, as expected, higher feed rates meant lower leach efficiencies (Figure 20) for two reasons. Firstly, with higher lead concentrations the leaching capacity of the AAS is reduced and secondly, the higher feed rates result in a higher AAS slurry density which causes fines to be washed out of the column sooner. Although the data are scattered, a weak trend is apparent. Also the higher feed rates resulted in a greater proportion of the feed reporting to the column sinks (Figure 21). This was unexpected because as the feed rate was increased, the slurry density of the AAS should increase resulting in a greater buoyancy effect and thus less feed material reporting to the sinks. It is difficult to determine the reason this was not so, but likely it was a "crowding" phenomenom between the end of the feed tube and the choke which caused lead compounds to be forced through the choke or a "clumping" of the pastes with metallics, giving the "lump" sufficient density to allow it to enter the trap with the rest of the metallics.

Thus, there is a direct trade off between current efficiency (also energy consumption) and leach efficiency. The 50 to 75 g/min range gives approximately 50% recovery with reasonable current efficiencies, so 60 g/min was used in subsequent runs.

FIGURE 18. RUN 2: STEADY STATE LEAD CONCENTRATION

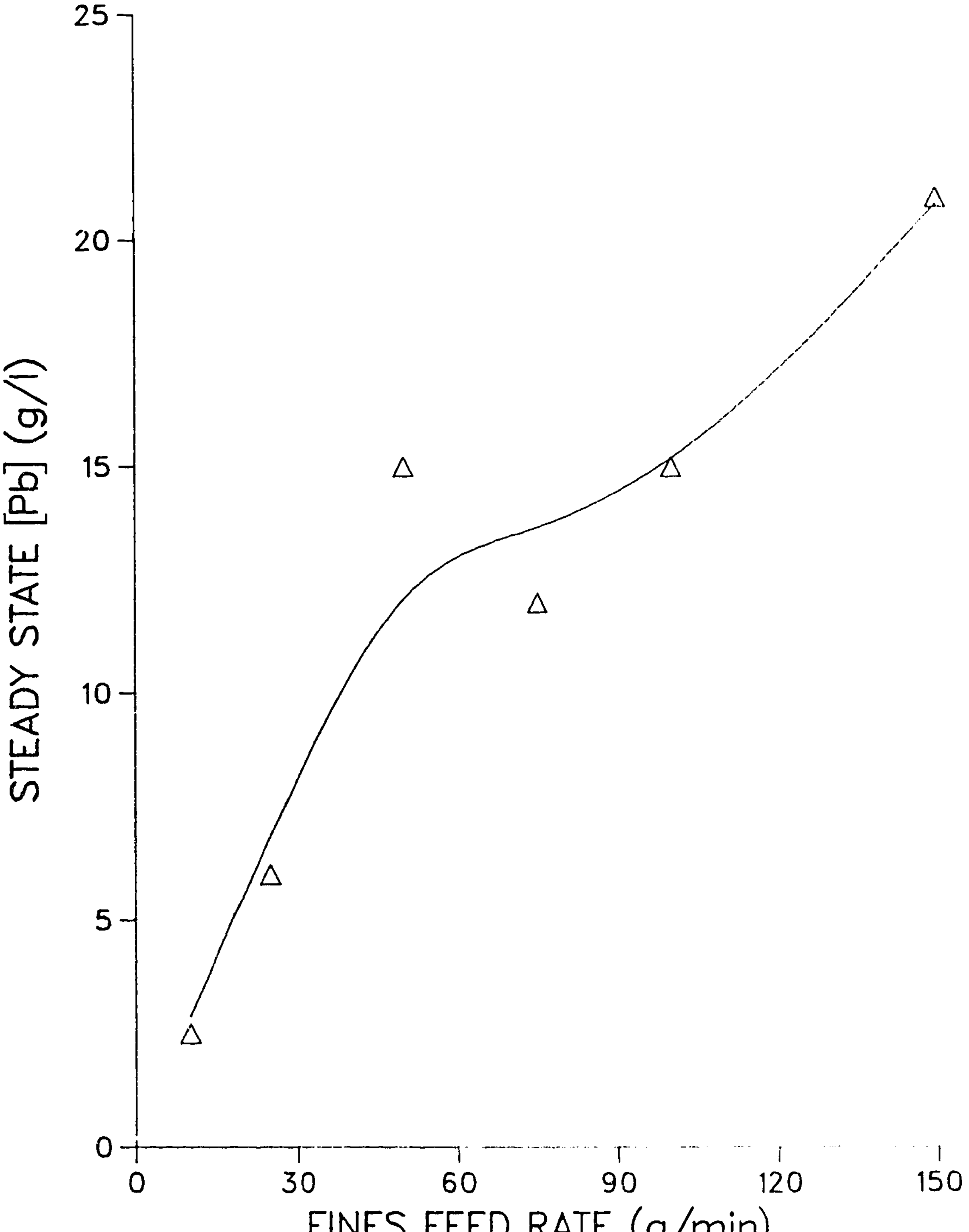


FIGURE 19. RUN 2: CURRENT EFFICIENCY

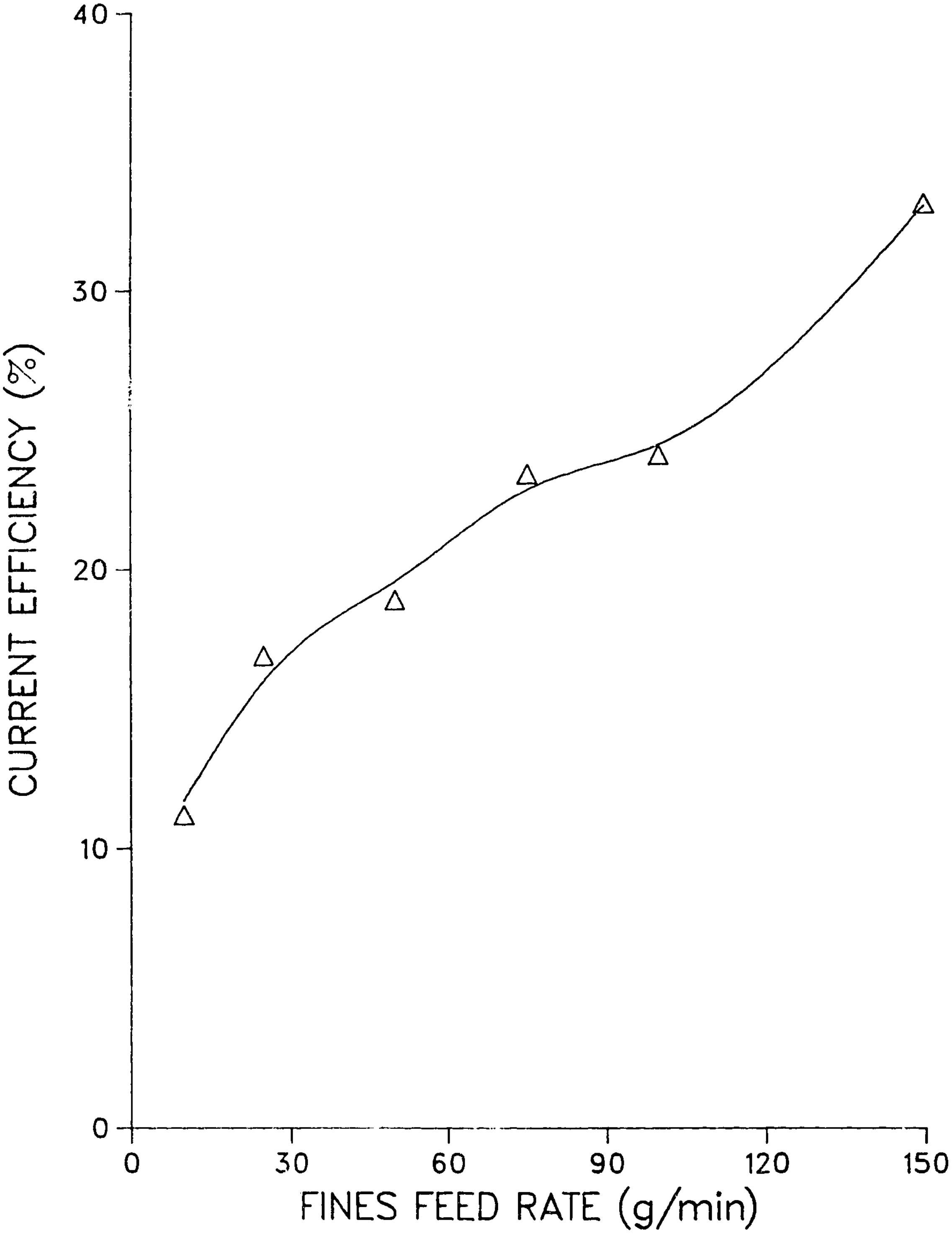


FIGURE 20. RUN 2: LEACH EFFICIENCY

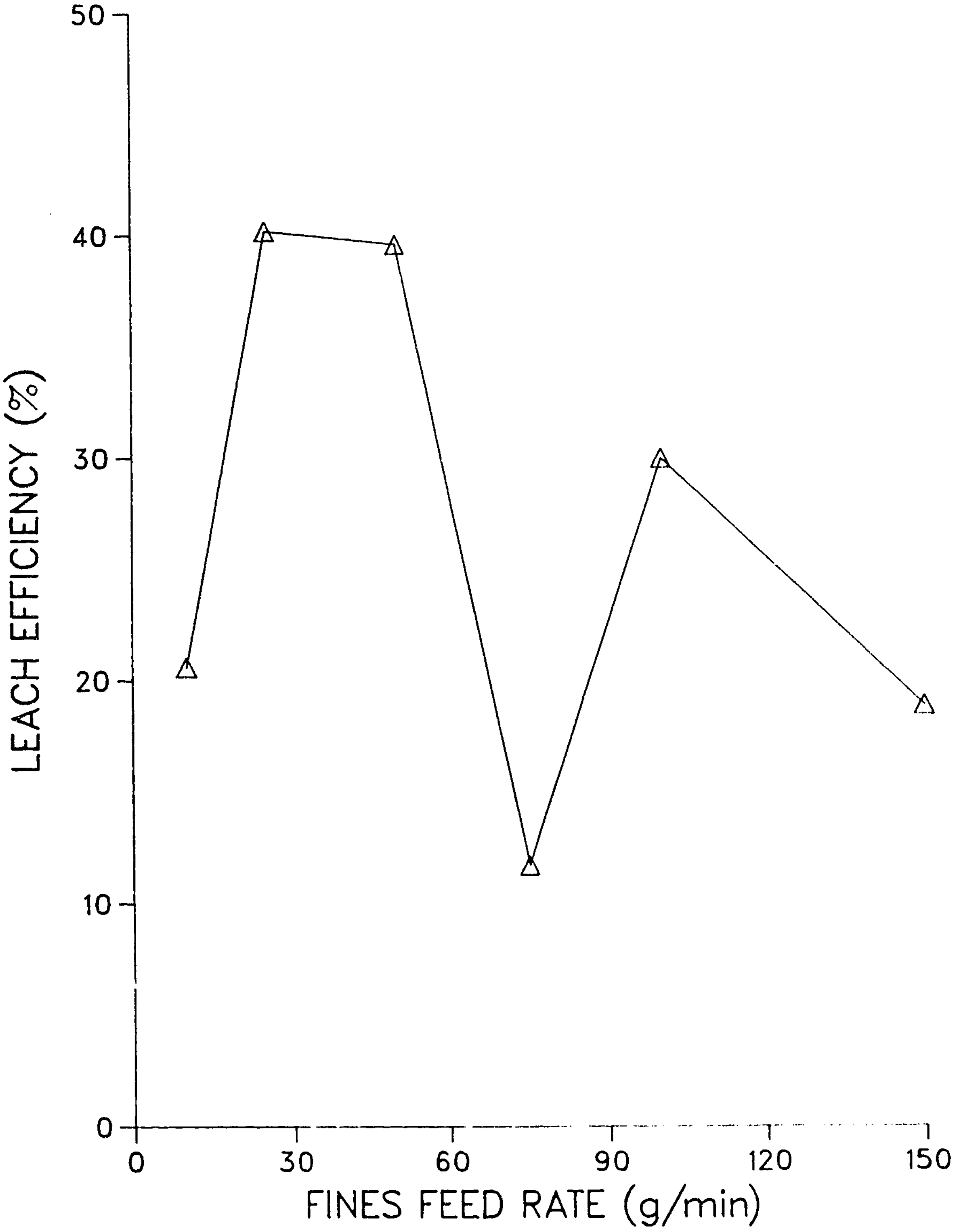
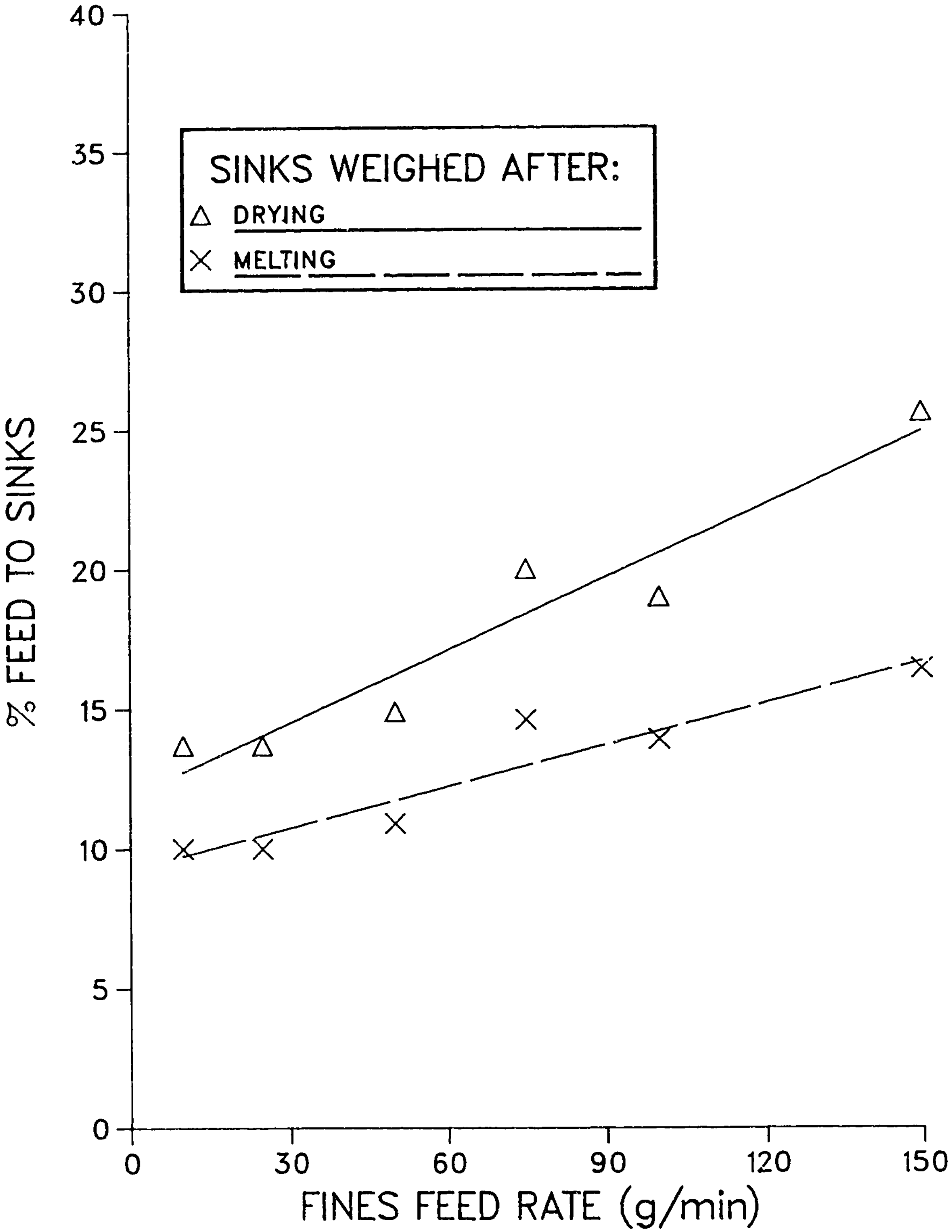


FIGURE 21. RUN 2: PERCENTAGE OF FEED REPORTING TO SINKS



Run 3: Ammonia Feed Rate

This third set of runs explored the effect of NH_3 feed rate (and thus NH_3 concentration) on the system's performance. The NH_3 feed rate was not measured directly, but was set by adjusting the NH_3 valve for low, low to moderate, moderate and high NH_3 feed (set according to the amount of rumbling in the leach column caused by collapsing NH_3 bubbles as the NH_3 dissolved). The total NH_3 used was then determined by weighing the NH_3 cylinder. The average feed rates tested were 17, 21, 118 and 246 g/min. For each of the first three runs, the NH_3 was started 15 minutes before the fines feeding and electrowinning power were started. This was to help stabilize the NH_3 concentration at the start of each run. For the fourth run, the NH_3 feed, fines feed and electrowinning power were started simultaneously. During the fourth run, the NH_3 feed had to be severely curtailed for the last 1/2 hour of the run. The solution was becoming saturated with NH_3 which caused NH_3 bubbles to rise up the feed tube, spraying AAS out over the top of the leach column. The 246 g/min is the average over the full 2 hours.

For this and subsequent runs, a major alteration was performed to the electrowinning tank. The three stirrers used until this run were removed and a baffle system was installed. A lucite plate was installed below every second electrode and above all the others, blocking the AAS from flowing through underneath or over the top of each electrode, respectively. This forced the solution to flow through each "cell", one after the other, in a weaving pattern through the electrowinning tank (Figure 22). Also, for these and all future runs, eleven electrodes were used for electrowinning, providing 10 cathodes and 10 anodes.

All runs were operated with a fines feed rate of 60 g/min, AAS flow rate of 9 l/min and a plating current of 50 amps. The column sinks for each run were not collected individually.

As can be seen in the graphs, the final (or "steady state") NH_3 concentration was directly related to the NH_3 feed rate (Figure 23). The NH_3 feed rate showed little effect on the steady state lead concentration (Figure 24) and therefore little effect on the current efficiency (Figure 25) or leach efficiency (Figure 26). Evaporation losses of NH_3, however, increased dramatically as NH_3 feed rates increased (Figure 27). It was apparent that, as long as sufficient NH_3 was present in the AAS, increased NH_3 feed rates had little effect on the system other than the rate of NH_3 evaporation. Thus, the low NH_3 feed rates appeared sufficient.

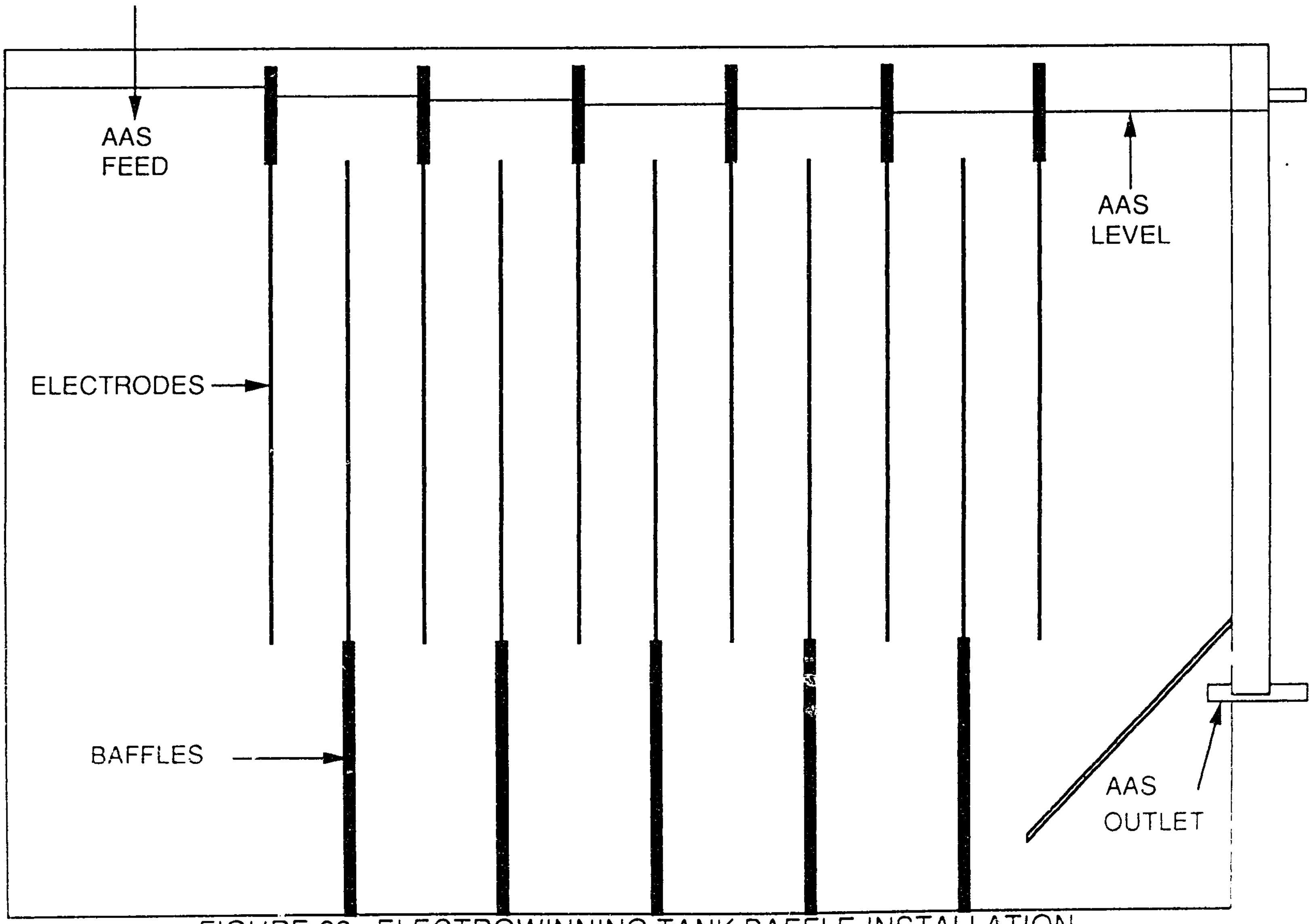


FIGURE 22. ELECTROWINNING TANK BAFFLE INSTALLATION

FIGURE 23. RUN 3: FINAL AMMONIA CONCENTRATION

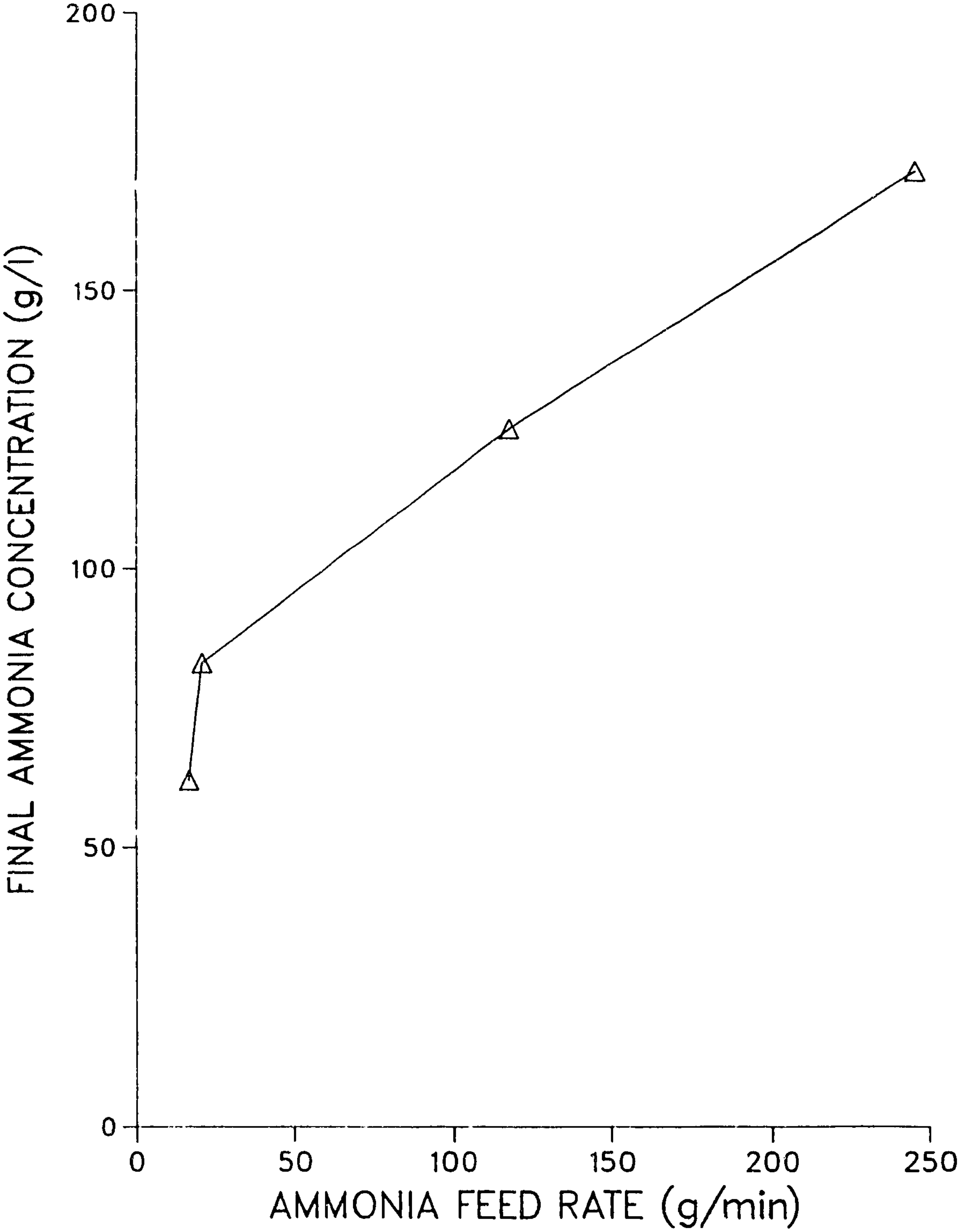


FIGURE 24. RUN 3: STEADY STATE LEAD CONCENTRATION

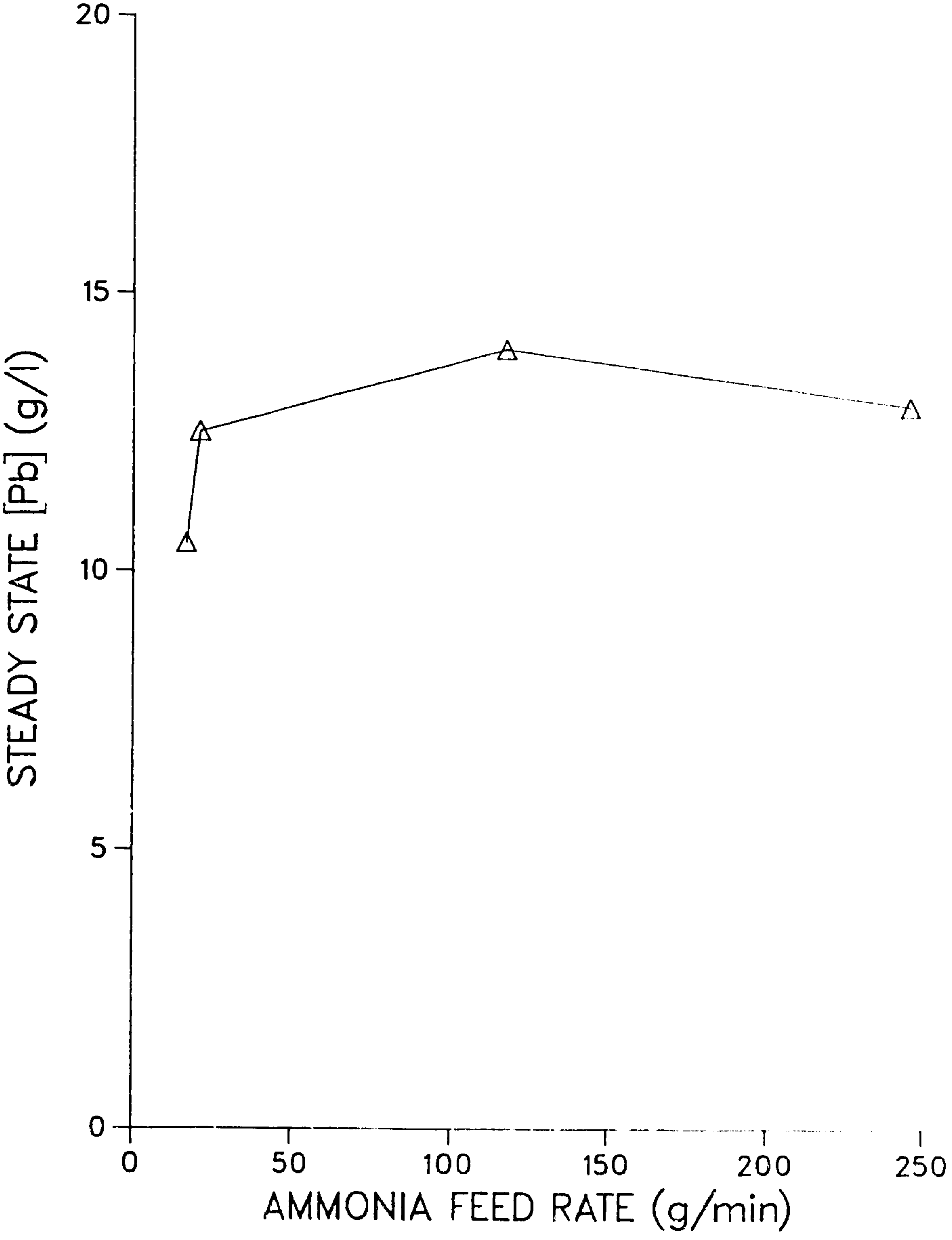


FIGURE 25. RUN 3: CURRENT EFFICIENCY

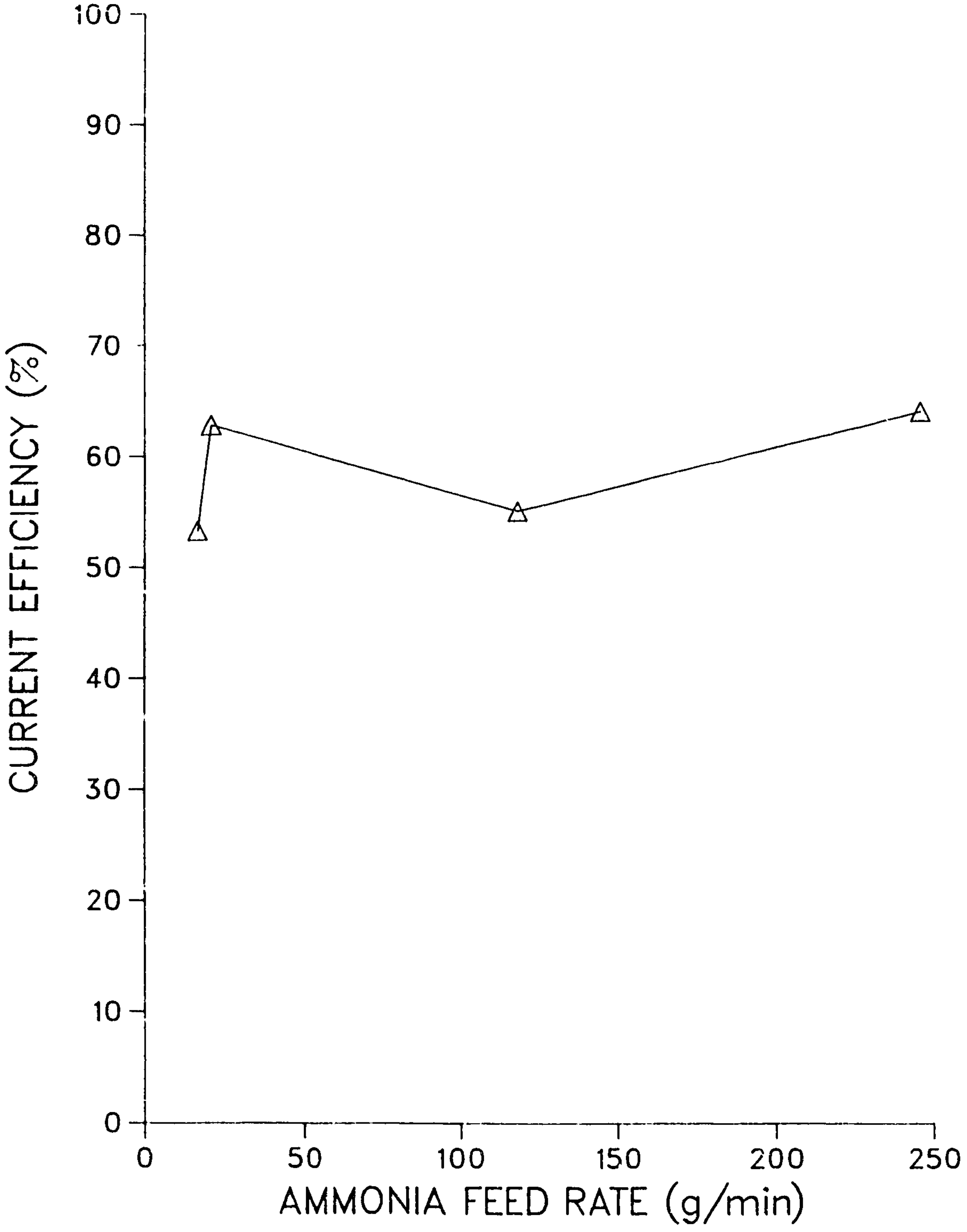


FIGURE 26. RUN 3: LEACH EFFICIENCY

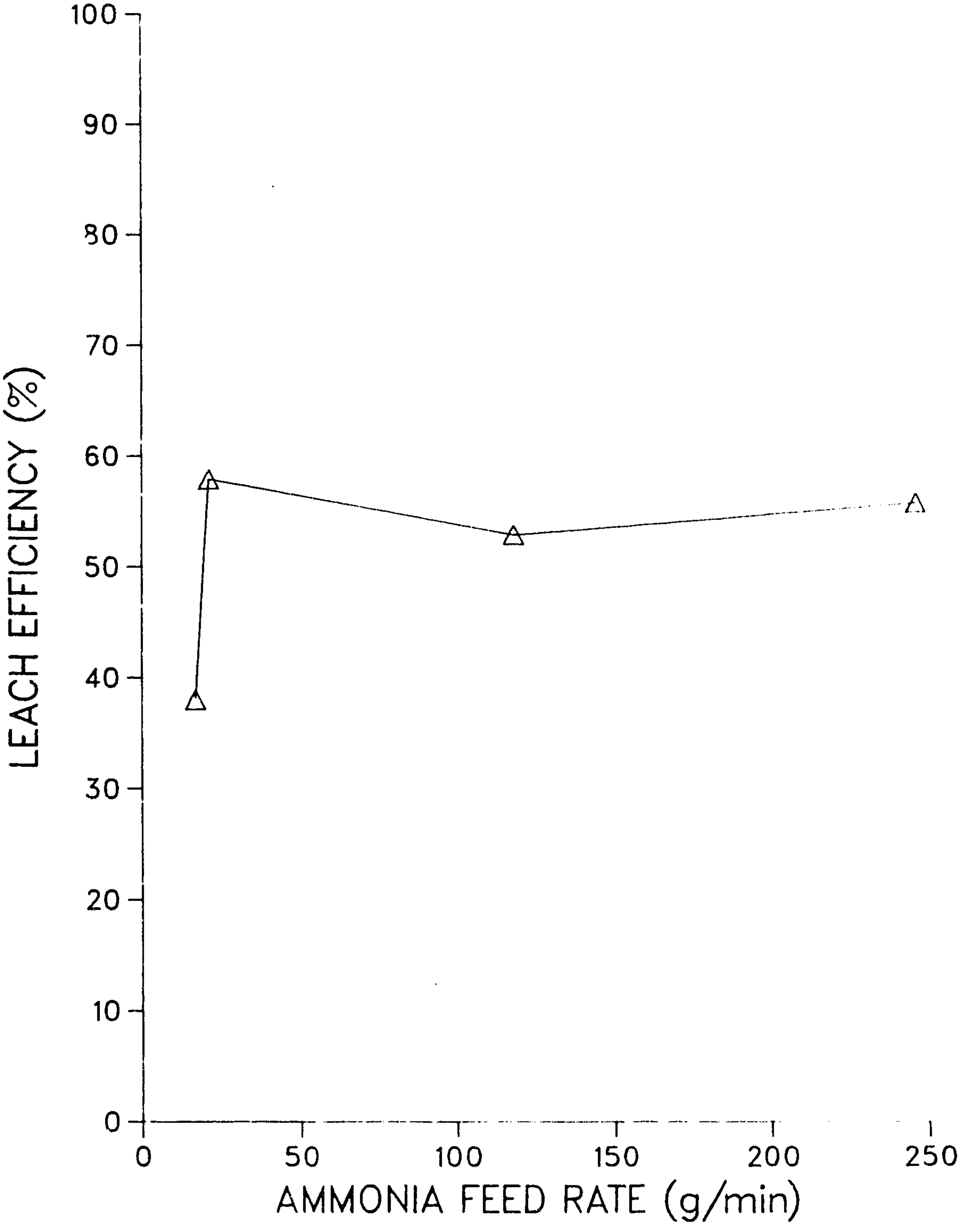
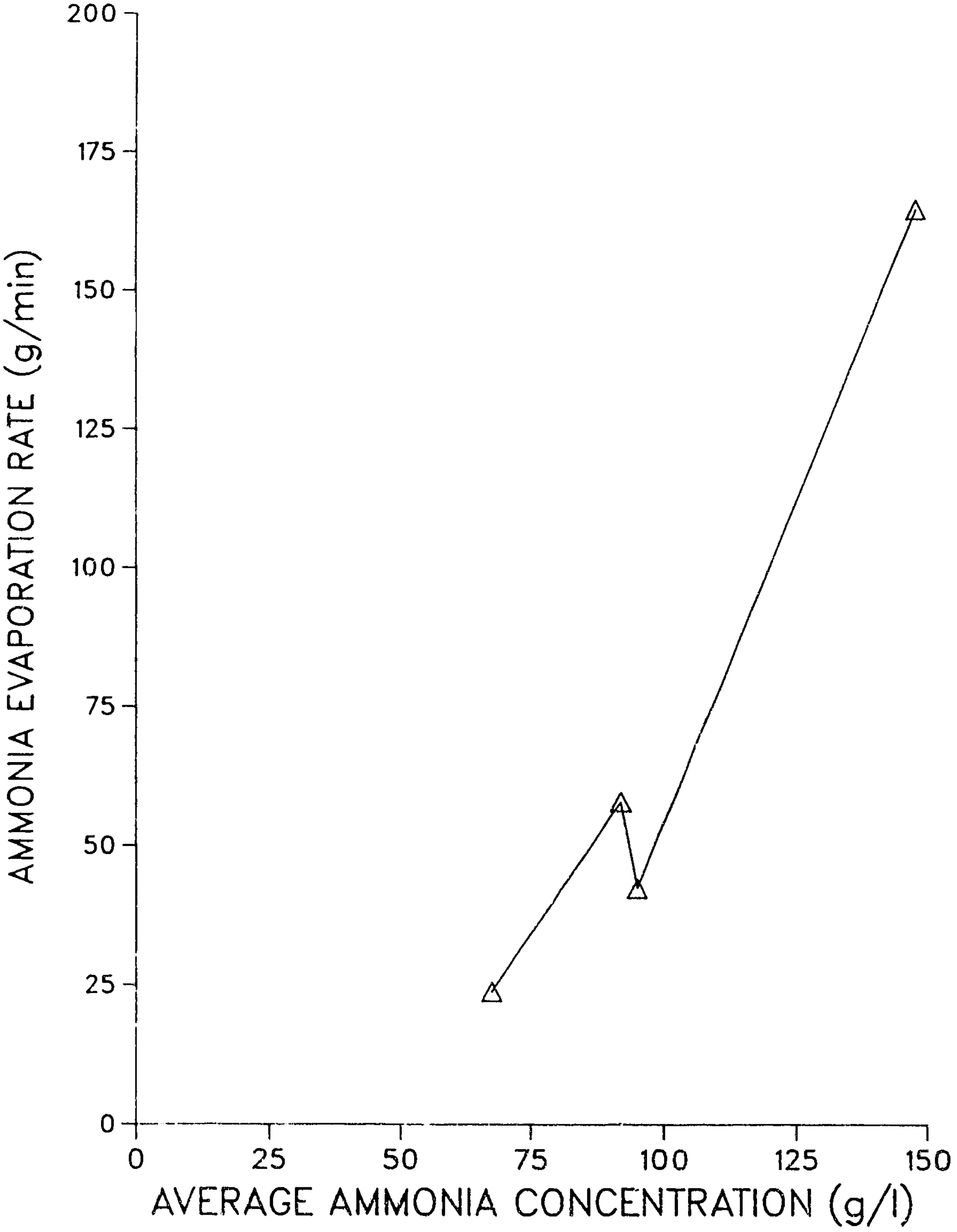


FIGURE 27. RUN 3: AMMONIA EVAPORATION RATE



Run 4: AAS Flow Rate

The fourth set of runs investigated the effect of the AAS flow rate on the metal separation efficiency as well as on the overall system performance. The flow rates investigated were 7, 9, 11 and 13 litres per minute. The plant set up was the same as that used in the third set of runs. The fines feed rate was 60 g/min, the plating current was 50 amps and the NH_3 feed rate was between 13 and 20 g/min except for the 11 l/min run where it was 104 g/min. For each run the power, fines feeding and NH_3 feed were all started simultaneously.

For each of the four runs, the leaching column sinks were recovered individually to allow assessment of the efficiency with which the metallics were being separated from the oxides and sulphate. The AAS flow rate was determined, as before, by directing the settling tank overflow into a 1000 ml beaker for a measured length of time. The volume recovered was then measured in a 1000 ml graduated cylinder. The flow rate was initially set as close to the desired rate as possible (by adjusting the pump speed w[illegible]riac) and left at that setting for the entire exp[illegible] The flow rate was again measured at the end of the [illegible]ment. Only with the 13 l/min run was there a substantial difference between the initial and final flow rates. This appeared to be caused by the AAS temperature increasing during the run (electrical resistance in the electrowinning section heated the solution to approximately

50°C during the run) which made the tygon tubing more flexible. At this high flow rate the suction created by the pump caused the tygon tubing to collapse somewhat, restricting the flow. It is also quite possible that during this run a lobe broke off of the pump impeller.

There is no correlation between current efficiency and AAS flow rate (Figure 28). The leach efficiency was reduced by higher AAS flow rates (Figure 29), most likely through higher carryover of fine paste material into the settling tank. The percentage of feed reporting to the sinks was not affected dramatically (Figure 30), while Figure 31 shows that the weight lost during melting decreased with increased AAS flow rates. In other words, a cleaner separation of the metallics in the feed material was effected by higher AAS flow rates.

FIGURE 28. RUN 4: CURRENT EFFICIENCY

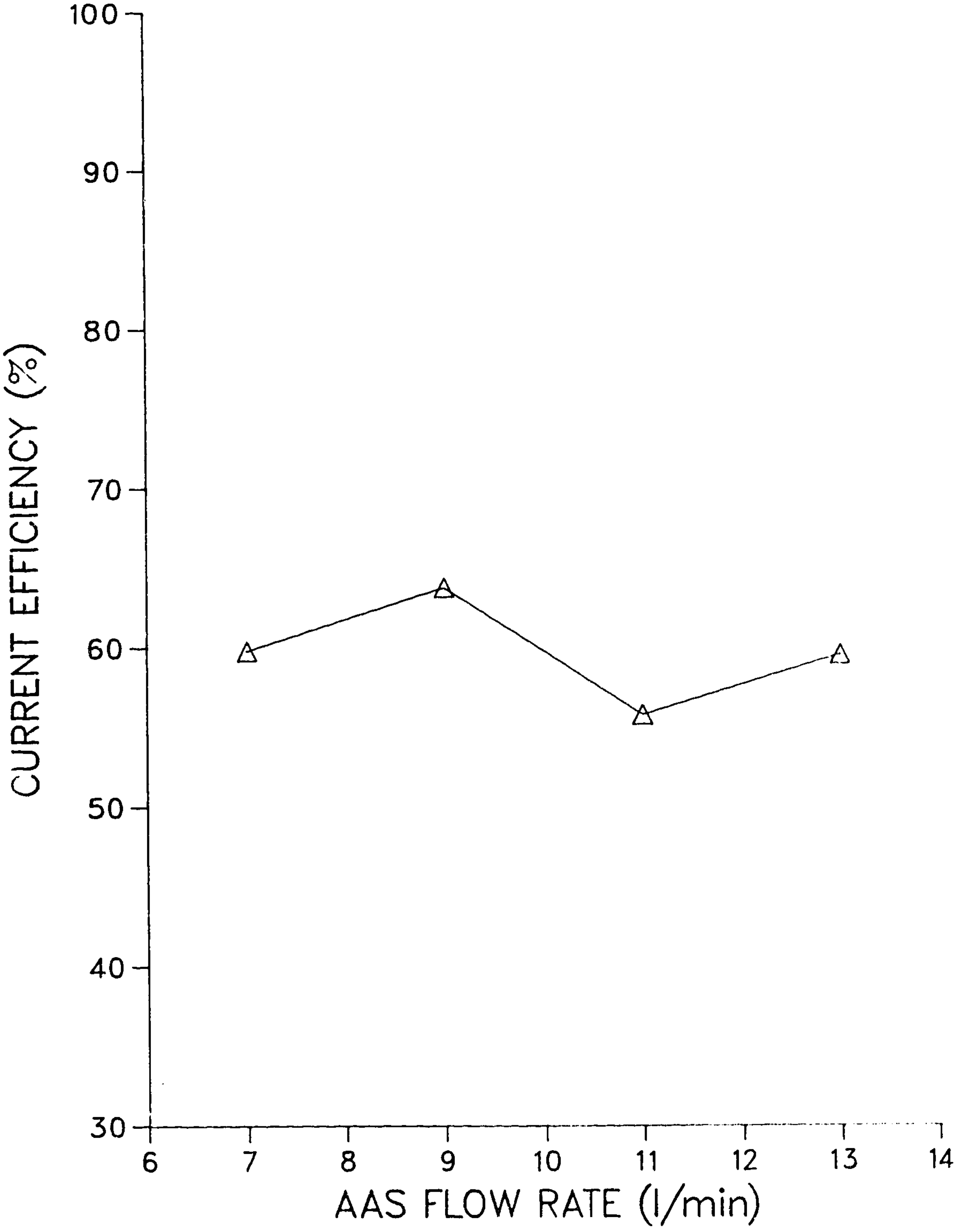


FIGURE 29. RUN 4: LEACH EFFICIENCY

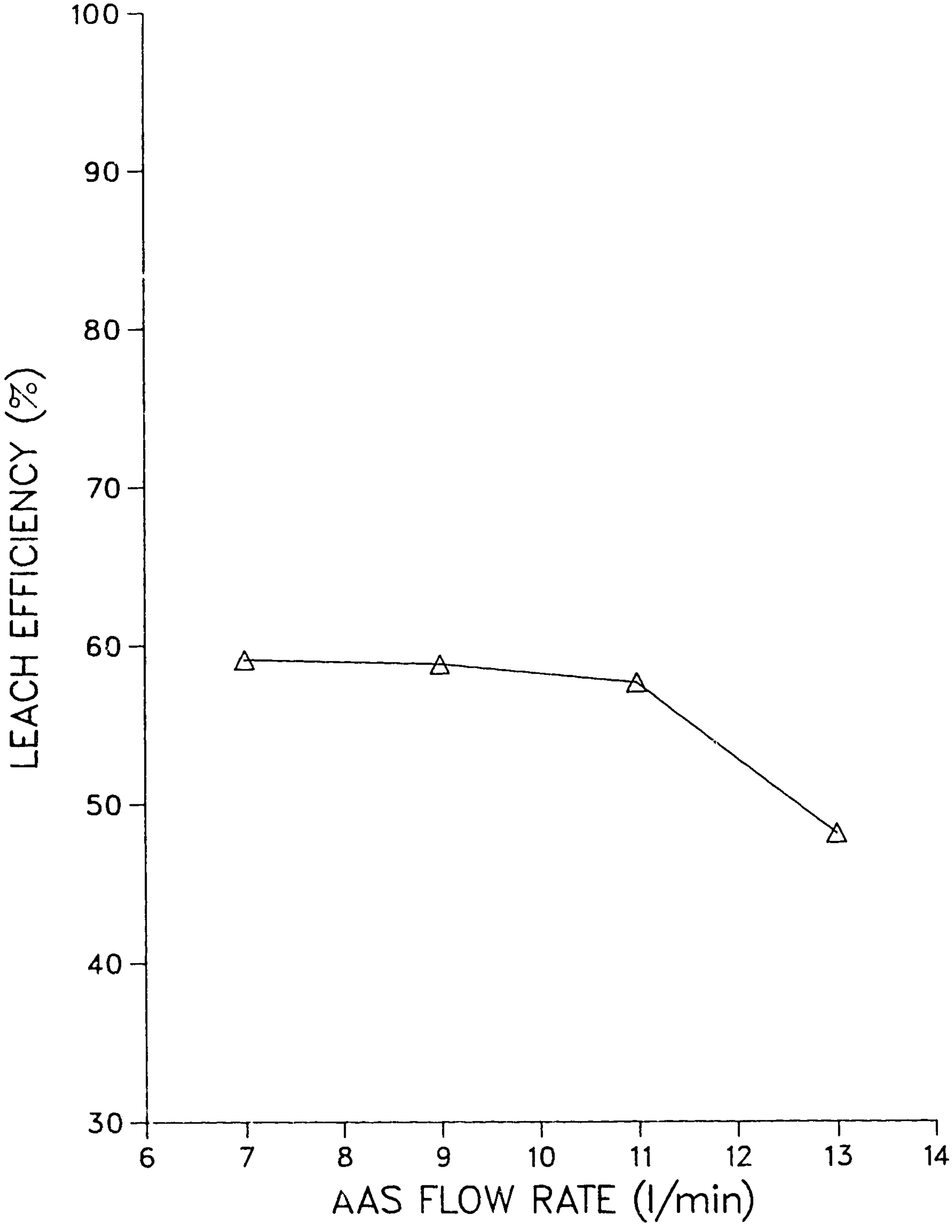


FIGURE 30. RUN 4: PERCENTAGE OF FEED REPORTING TO SINKS

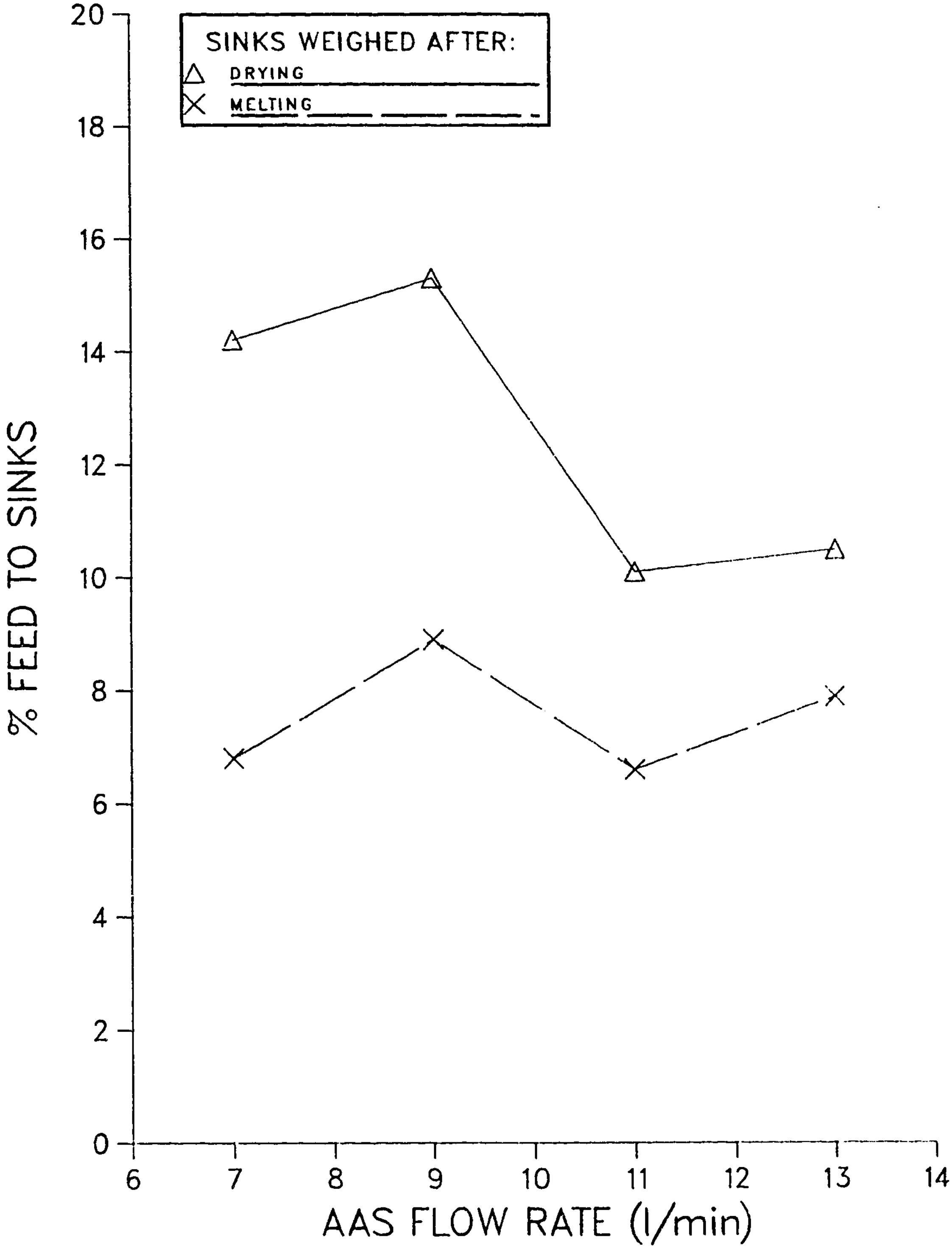
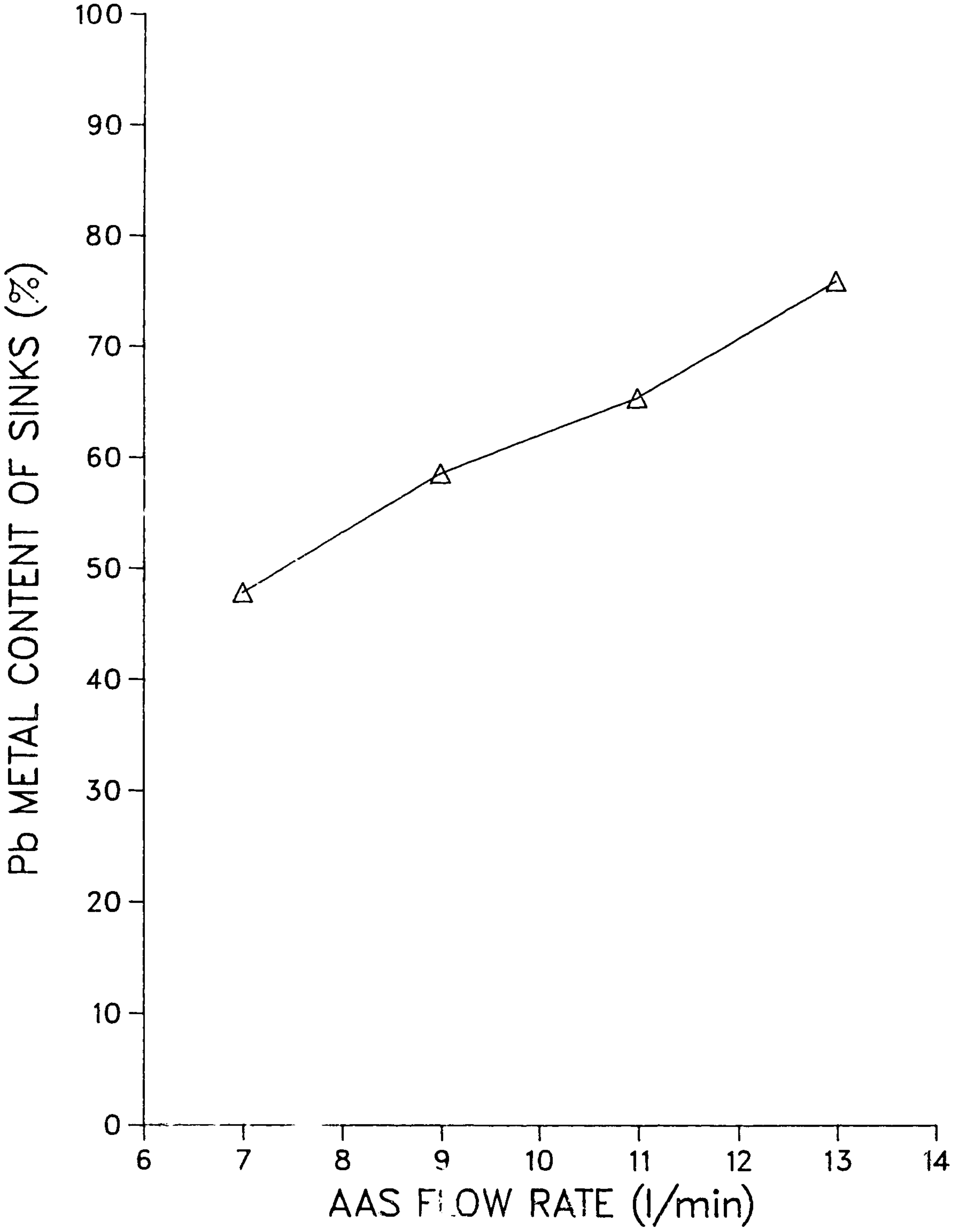


FIGURE 31. RUN 4: SINKS CLEANING EFFICIENCY



Run 5: Additives

Run 5 was an investigation into the effects of organic additives on leaching and electrowinning. Sugar and cationic polyacrylamides were the two additives investigated as their use was mentioned in the literature. Sugar was used to improve the leaching characteristics of the alkaline solution used in the *Plombrec Process*[1] and cationic polyacrylamides were mentioned by Bratt and Pickering with reference to improving lead electrowinning in the *AAS Process*.[130] Cationic polyacrylamides are also used as floculating agents; thus, the added benefit of better clarification in the settling tank was anticipated.

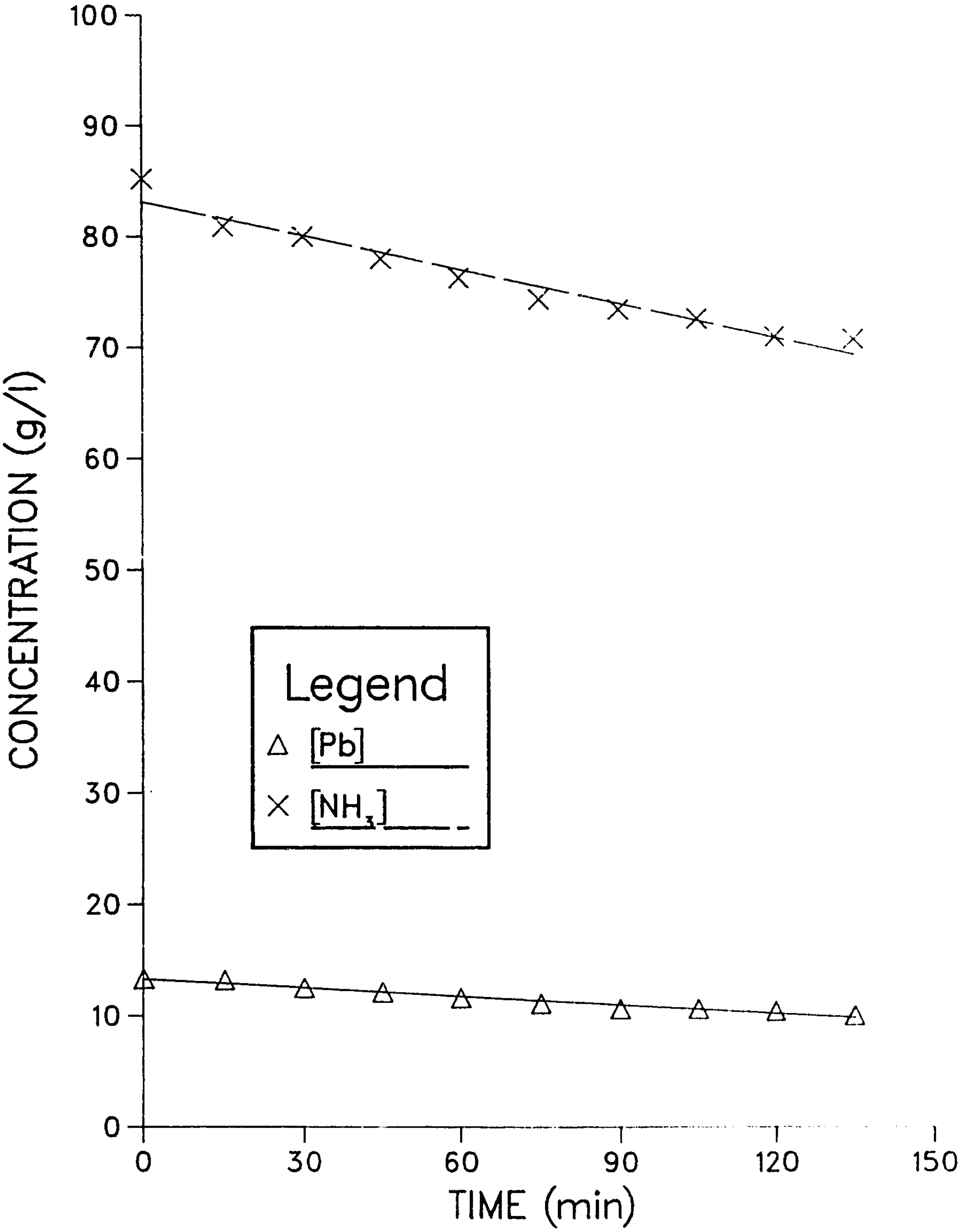
For this run, the additives were introduced as follows:

Table 6. Organic Additives Tested.

Time (min)	Additive	Concentration (ppm)
0	12.5 g sugar	100
30	112.5 g sugar	1000
60	6.25 g Polyhall 361 (Celanese)	50
90	6.25 g Reagent S-3732 (Cyanamide)	50
120	6.25 g Separan CP7 (Dow)	50

The run was accomplished using the same setup as in Run 3. The AAS flow rate was 9.5 l/min, the NH_3 feed rate was 27 g/min, the plating current was 50 amps and the fines feed rate was 60 g/min. At 1/2 hour intervals, the chemical additive was mixed with approximately 300 ml distilled water and added to the leach column through the fines feed tube. The nature of the lead deposit on the cathodes was then watched closely to see if any changes occurred. No difference in the lead deposit nor in any operating parameter of the system was noticed for any of the additives. No unusual change in the lead concentration or the NH_3 concentration occurred with any of the additives (Figure 32). The final three reagents (not the sugar) each produced a small amount of froth in the electrowinning tank. In all three cases, it was gone within the 1/2 hour. The only other difference noticed was that the crystalline precipitate recovered during evaporation (for $(NH_4)_2SO_4$ analysis) turned brown. This was likely due to the sugar in the sample "burning" in the drying oven. The current efficiency of 52%, energy consumption of 1.34 kWh/kg and the leach efficiency of 42% were all typical for the parameters used in this run.

FIGURE 32. RUN 5: LEAD AND AMMONIA CONCENTRATIONS



Run 6: Sulphuric Acid Pretreatment

These runs examined the efficiency with which the lead oxides can be converted into $PbSO_4$ with H_2SO_4. It has been determined that PbO_2 can be converted to $PbSO_4$ using concentrated H_2SO_4 at elevated temperatures.[163] The conversion rate increased with higher H_2SO_4 concentration and higher temperature.

The conversion was tried on ground battery fines as well as on the slimes recovered in the settling tank during previous runs.

For the settling tank slimes, 600 g of dried slimes was weighed into each of twelve 600 ml beakers and approximately 400 ml of 25% H_2SO_4 was mixed in to form a slurry. The beakers were then placed on a hot plate which held the temperature of the slurry at approximately 86°C for 10 hours.

For the battery fines feed material, 600 g of material was weighed into each of twelve 400 ml beakers and slurried with approximately 170 ml of 25% H_2SO_4. The beakers were left on the hot plate at approximately 80°C for 13 1/2 hours. (In both cases the temperature was not uniform throughout the beaker. The temperature was hottest at the bottom and coldest at the top; the temperature differential was as much as 20°C in some beakers.) For both materials the only change observed was a lightening of the brown color at the bottom of the beakers (where the temperature was the highest).

The treated material was used as feed for two runs; one run using the settling tank slimes and the other using the battery fines. Both runs used the same apparatus as in Run 3 with the plating current set at 50 amps. The lead material/H_2SO_4 slurry was fed directly into the leach column feed tube at the rate of 60 g/min (dry basis). For the battery fines, the AAS flow rate was 9 l/min and the NH_3 was fed at 39.7 g/min. For the settling tank slimes, the NH_3 feed rate was 25 g/min and the AAS flow rate was reduced to 7.5 l/min as this material was quite fine (having been already washed out of the leach column in previous runs) and had no metallics left in it.

For the battery fines, the resulting current efficiency, energy consumption and leach efficiency (53.7%, 1.26 kWh/kg and 57%, respectively) are typical for the battery fines material. H_2SO_4 pretreatment did not have a significant effect.

For the settling tank slimes, the current efficiency, power consumption and leach efficiency were 48%, 1.47 kWh/kg and 41%, respectively. As no control was used (i.e., a run with untreated slimes) the effectiveness of the H_2SO_4 treatment is not indisputable. It is encouraging, however, that 41% of the slimes were "recovered" by this run.

Run 7: Electrode Spacing

Run 7 determined the effect of the electrode spacing on current efficiency and energy consumption in the electrowinning system. Five runs were done with the electrodes spaced 1, 2, 3, 5 and 7 cm on center. To conserve feed material, runs were only 1 hour long and the system was operated at one fifth of its usual production rate. Thus, only 3 electrodes were used in the electrowinning tank (with baffles as described in Run 3) providing 2 cathodes and 2 anodes. The amperage setting was still 50 amps, but with only 2 cathodes the plating capacity was only 20% of the capacity with 10 cathodes. To compensate for the lower plating capacity, the battery fines were fed at 12 g/min as compared to the usual 60 g/min. For all runs the AAS flow rate was set at 9 l/min and the NH_3 feed rate averaged 60.5 g/min.

For these runs, the battery fines feed material was again pretreated with H_2SO_4. 240 g of fines was weighed into fifteen 400 ml beakers and slurried with 200 ml of 30% H_2SO_4. The beakers were then left for 12 hours on a hot plate which maintained the slurry temperature at approximately 85°C. During the runs, the slurry was fed directly into the leach column feed tube, each beaker over a 20 minute period, to obtain the desired 12 g/min (dry basis) feed rate.

The effects of electrode spacing on current efficiency and energy consumption are shown in Figures 33 and 34.

Electrode spacing had very little effect on current efficiency, although the current efficiency did show an overall tendency to increase with increased electrode spacing. This is to be expected as the closer the electrodes are, the more short circuiting would be experienced when the electrodes were scraped (with a metal scraper). At the 1 and 2 cm spacings, the cathodes had to be scraped continuously to prevent the deposit from short circuiting the cells (by bridging the space between the anodes and cathodes). As expected, the power consumption increased with larger electrode spacing due to the higher voltage required to maintain the 50 amp current.

Leach efficiencies in the 70% to 85% range were experienced, which was much higher than usual. This is likely due to the lower feed rate (as seen before in Run 2).

Unfortunately, the energy savings at the 1 and 2 cm spacings were offset by the difficulty in scraping the electrodes and keeping the deposit from short circuiting the electrodes (this problem would be compounded if all 11 electrodes were used). Thus, subsequent runs continued to use the 3 cm electrode spacing. This provides the narrowest spacing (thus lowest energy consumption) that can be used while still providing easy access for scraping the cathodes.

FIGURE 33. RUN 7: CURRENT EFFICIENCY

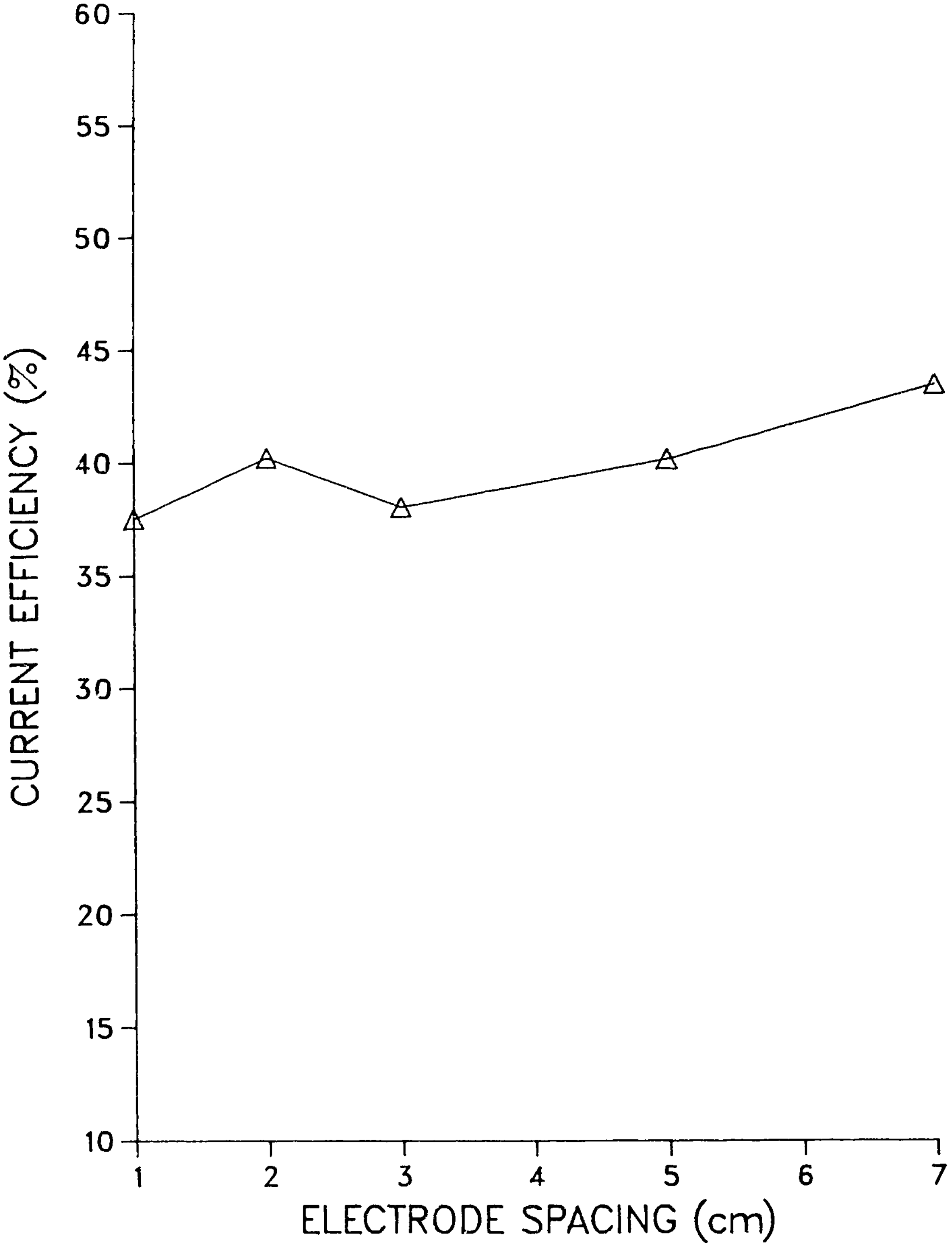
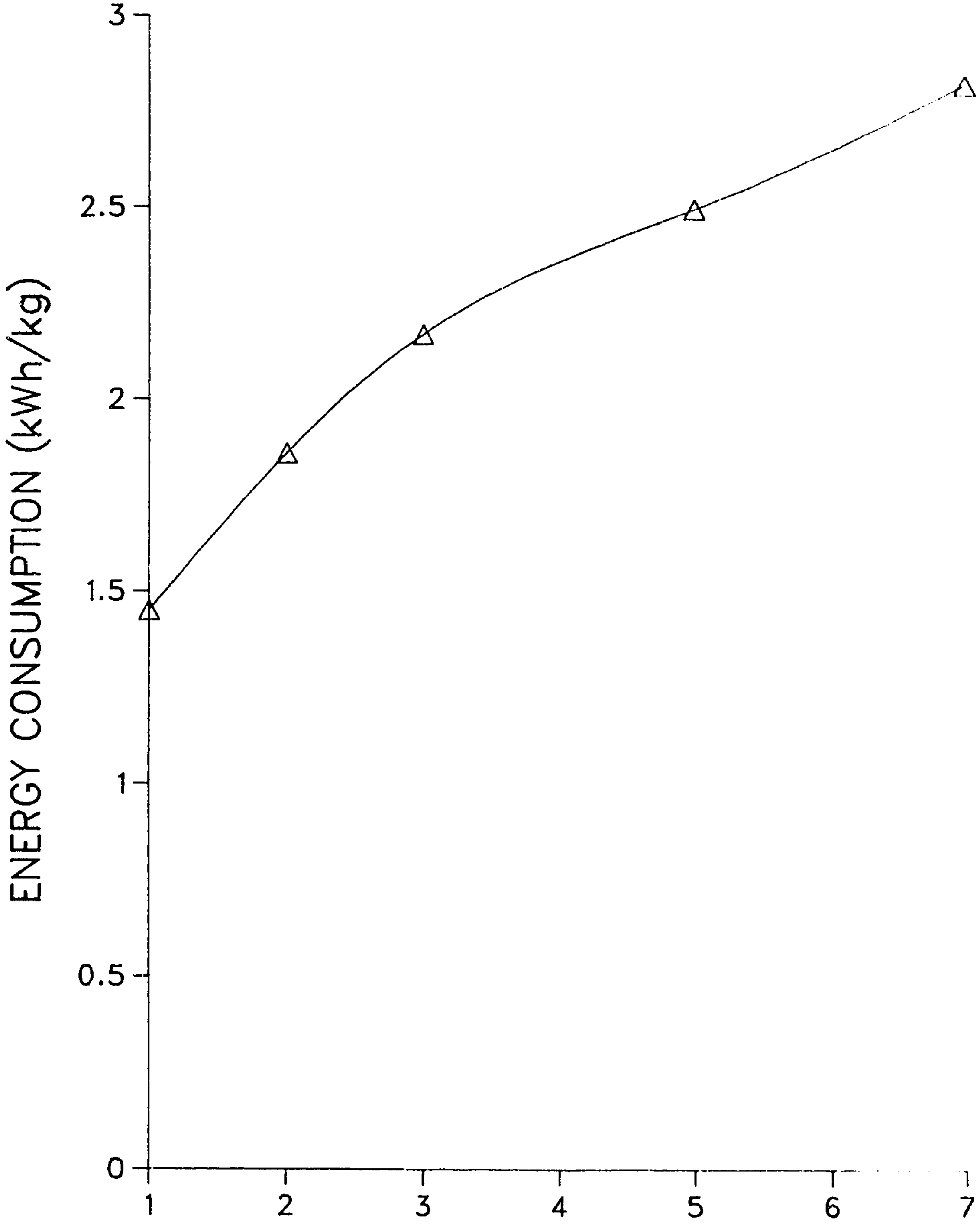


FIGURE 34. RUN 7: ENERGY CONSUMPTION



Run 8: Electrowinning Voltage and Current

The eighth set of runs provided the opportunity to try to increase current efficiency by decreasing the current density (by smaller increments than used in Run 1) and to try to increase the leach efficiency by again pretreating the feed material, this time with more concentrated H_2SO_4.

The three runs were performed at 25, 35 and 50 amps (3.1, 4.4 and 6.3 amps/sq dm, respectively). For all three runs the same setup as with Run 3 was used with the AAS flow rate at 9 l/min, the electrodes spaced 3 cm on center, the battery fines feed rate at 60 g/min and an average NH_3 feed rate of 60 g/min.

H_2SO_4 pretreatment of the feed was accomplished by weighing 600 g of battery fines into twelve 600 ml beakers for each run. The fines were then slurried with approximately 300 ml of 50% H_2SO_4 and placed on a hot plate at 100°C for 12 hours. During each run the slurry was fed directly into the leach column feed tube at the rate of one beaker every 10 minutes.

The H_2SO_4 pretreatment appeared to be effective in converting the PbO_2 to $PbSO_4$, as the slurry color changed from brown to grey/white over the 12 hour period. This did not seem to affect the leach efficiency, however, as it was still in the 50% to 60% range (Figure 35).

Current efficiencies, on the other hand, were greatly increased (Figure 36) and energy consumption decreased (Figure 37) with the decreased current density.

FIGURE 35. RUN 8: LEACH EFFICIENCY

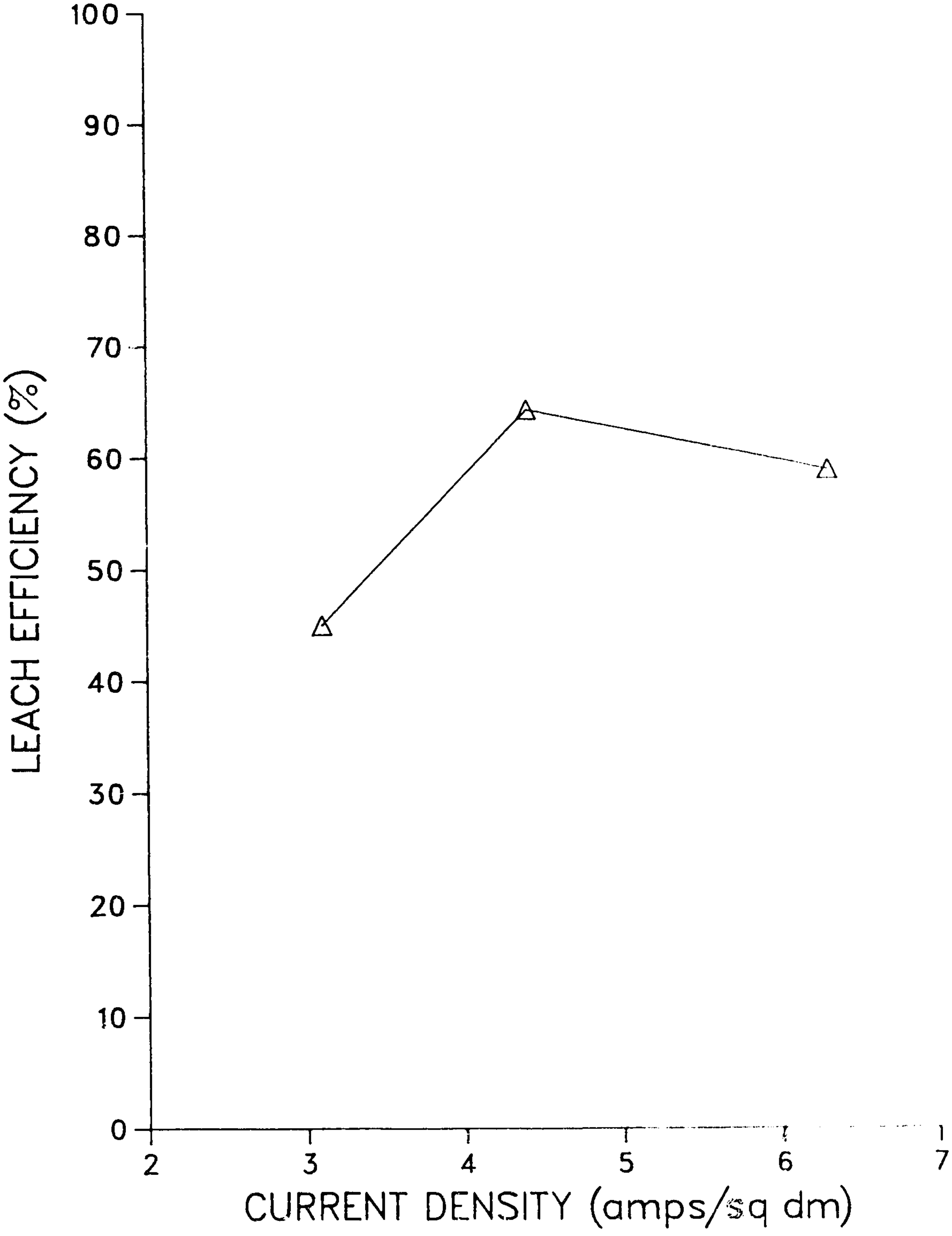


FIGURE 36. RUN 8: CURRENT EFFICIENCY

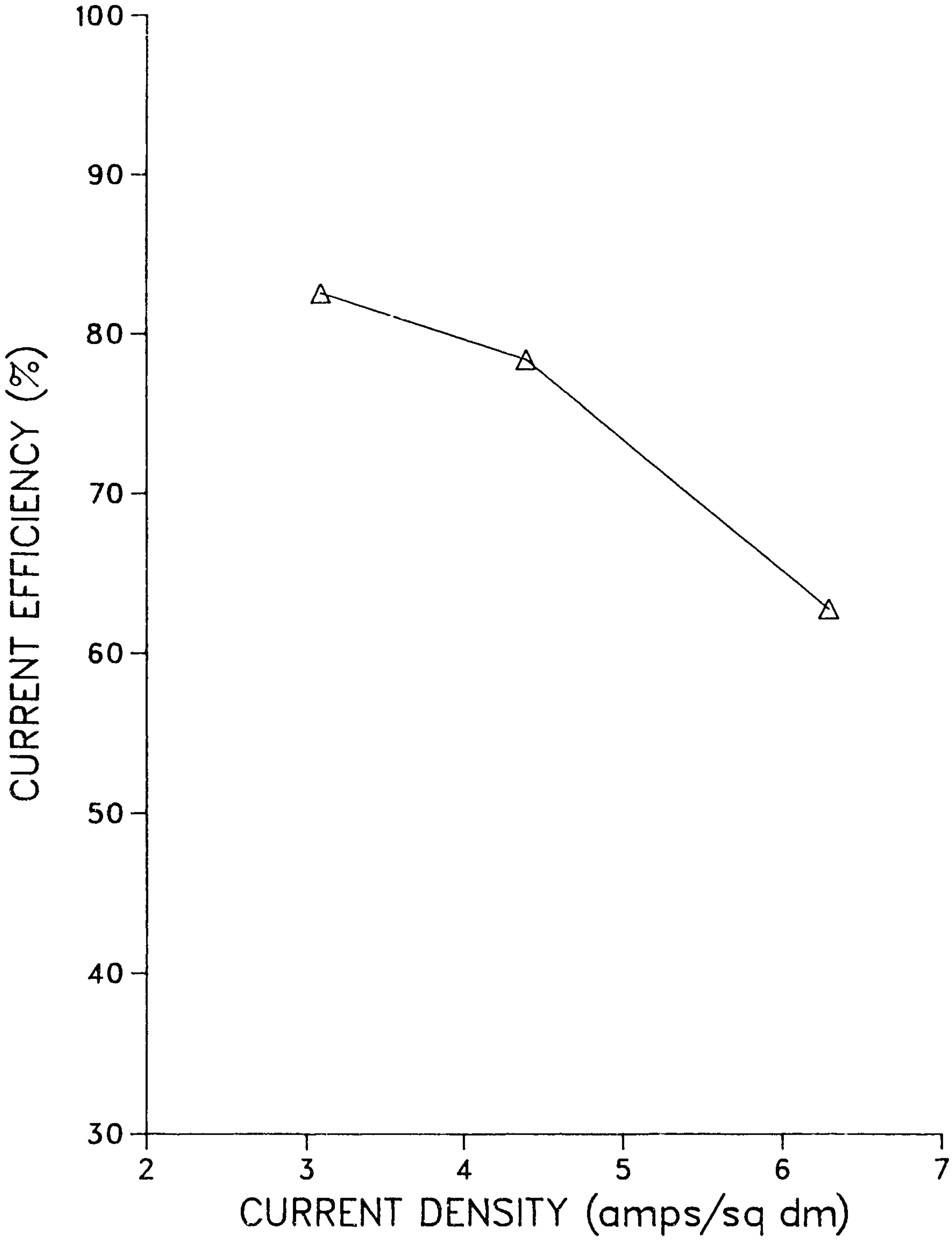
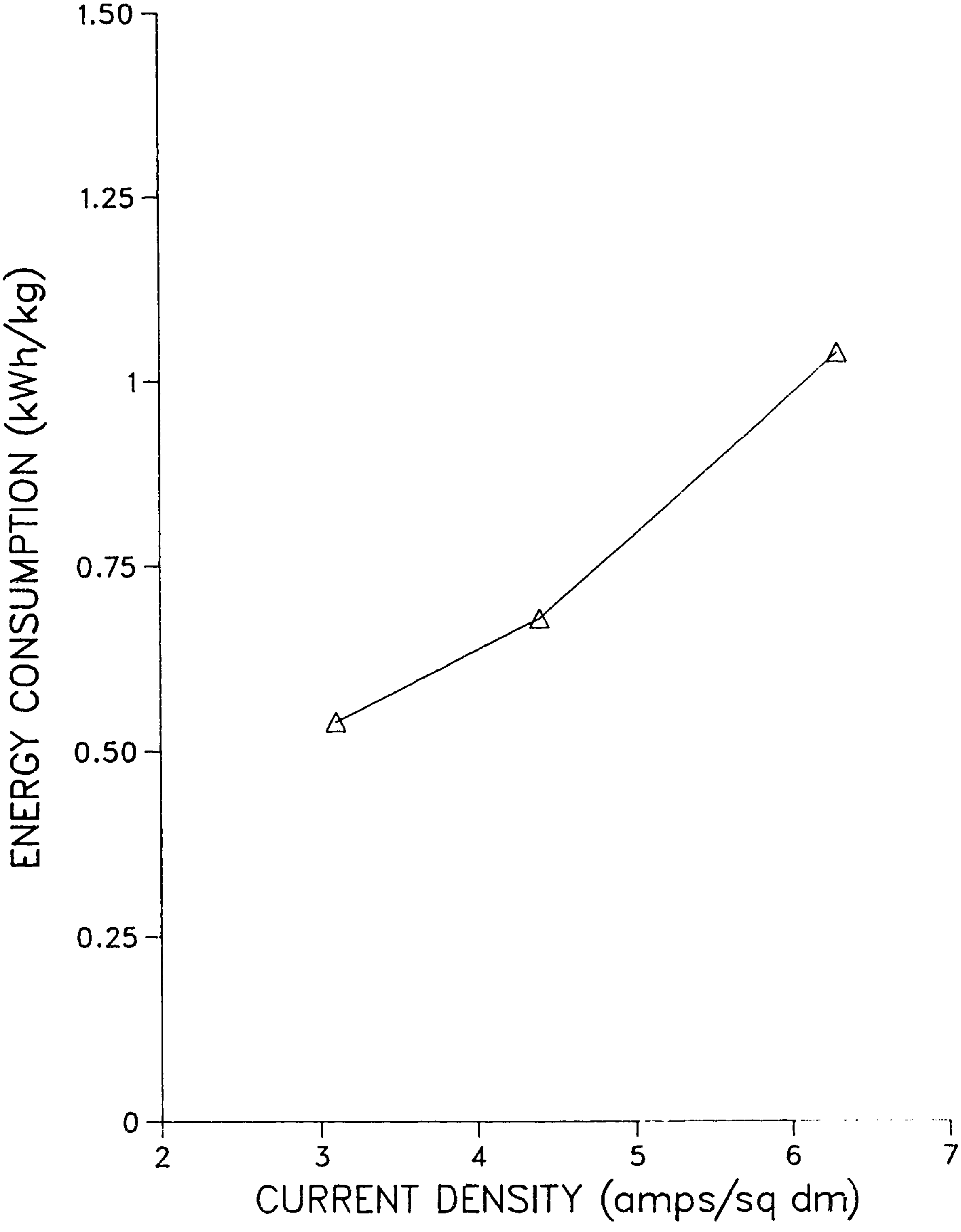


FIGURE 37. RUN 8: ENERGY CONSUMPTION



Run 9: Final Run

The pilot plant was operated for a final 2 hour run with the operating variables set for optimum performance,. as determined by the previous runs.

Complete battery plates were used for this run, to provide a more realistic feed material (i.e., the large pieces of grid metal were not removed before grinding - the separators and plastics were still removed by hand). The plates were ground in a laboratory ball mill for 1 hour per charge (7 kg). During this milling some of the grids disintegrated while some simply "balled up". The feed was screened with a 6.4 mm screen to remove the large pieces of grid material as they would plug the choke in the leaching column. These pieces comprised 13.6% (by weight) of the original material. Of the screened fines a sample was washed and a gravity separation performed to determine the proportion of metallic lead in the fines (in previous runs it was much lower because the large pieces of grid metal were manually removed from the feed before grinding). The metal content was approximately 33%. Thus, to ensure a lead oxide/sulphate feed rate of 60 g/min, the feed rate for this material was increased to 90 g/min. Nine hundred grams of fines were weighed into each of twelve 600 ml beakers and slurried with approximately 300 ml of 50% H_2SO_4 then set on a hotplate for 12 hours at 100°C. The color of this material after pretreatment was a sightly lighter brown, but did not change to the grey/white color as did the feed for Run 8.

The same setup as in Run 3 was used with the 3 cm electrode spacing, 9 l/min AAS flow rate and a current setting of 30 amps (3.9 amps/sq dm). The fines feed rate of 90 g/min (dry basis) was obtained by feeding each beaker of fines/H_2SO_4 slurry directly into the leach column feed tube over a 10 minute period. The NH_3 feed rate was 21 g/min.

The results obtained for this run (the proportion of grids in the feed that were removed by screening, have been added back into the feed and assumed to report to the sinks) showed a current efficiency of 76%, an energy consumption of 0.65 kWh/kg and a leach efficiency of 26%. Comparison of this run with Run 8 clearly shows the effect of increased fines feed rate on leach efficiency.

VII. DISCUSSION

A. SOURCES OF ERROR

When analyzing the data obtained from operating the pilot plant, it is important to keep in mind the various ways errors can arise both in obtaining the data and in analyzing it. In operating a pilot plant, much more difficulty is experienced in controlling the process than when individual tests are conducted in beakers. This is due to the much larger scale involved as well as the fact that everything is happening simultaneously (which tends to keep the operators busy). Problems must be rectified while the plant continues to operate if the data obtained are to have any significance.

Perhaps the most important source of error in the tests occurred in the washing and melting of the cathode deposit. The deposit was always spongy and as such contained a large amount of AAS solution as well as very fine paste material (mostly PbO_2 which stayed suspended in the AAS throughout the system). The cathode deposit was first washed with NH_4OH to remove the leaded AAS without precipitating Pb_2OSO_4 (through dilution); then the deposit was washed with water to remove the NH_4OH, $(NH_4)_2SO_4$ and fine PbO_2. It was virtually impossible to remove all the PbO_2 and, as well, some of the fine cathodic lead was lost in the washing. Upon melting, any remaining PbO_2 would oxidize even more of the metallic lead (producing a PbO "slag"). It was decided that using the melted weight for calculations, giving a conservative value for the weight of cathodic lead, was preferable to using the weight of the dried deposit (with entrained $(NH_4)_2SO_4$ and PbO_2) which could possibly give a misleadingly high value. In a commercial operation, the weight of melted lead is what is important. Higher current efficiencies (for example) are of little use if they do not translate into a comparable amount of metallic lead. It is important to remember that errors resulting from washing and melting will have a greater significance for those runs where smaller quantities of cathodic lead are produced.

Other sources of error in electrowinning are the short circuiting of electrodes by the metal scraper used to remove the cathode deposit and by the cathode deposit itself (large lumps of cathode deposit were often circulating in the tank and easily lodged between electrodes). Short circuiting lowers the current efficiency as the conducted current is not available to reduce lead ions. It is interesting to note that short circuiting of a cell had no marked effect on the current or voltage readings for the electrowinning tank. Thus, a short circuit could not be detected simply by a sudden increase in current or decrease in voltage for the tank. In contrast, as the deposit built up on the cathodes, the electrowinning tank voltage would slowly decrease with a corresponding current increase. If the cathode deposit was allowed to build to any appreciable thickness, when it was removed there would be a dramatic voltage increase and a simultaneous drop in current. This introduced a certain amount of error in the current and voltage recorded, depending to what extent the cathode deposit had built up at the time the reading was taken.

Errors in the materials balance for each run are introduced by the pilot plant operation itself, as well as by assumptions made in the calculations. During some runs, AAS had to be removed to compensate for the volume of water entering via the feed slurry and/or to compensate for the volume increase from the NH_3 fed. This AAS removal, as well as any spillage which occurred, were not taken into account in the materials balance (the lead lost would be assumed to report to the settling tank slimes).

In the calculations themselves, all lead dissolved and electrowon is assumed to have entered the system as $PbSO_4$ (while, in fact, a portion would have entered as PbO). Also, for some sets of runs, some values were obtained only once and averaged over the set of runs (example: sinks for most runs were removed only after the set of runs was complete; it was assumed that each individual run contributed equally to the total). Finally, the steady state lead and NH_3 values were estimated and different values could be determined depending upon the starting point of the run. For example, with all other factors being equal, the steady state lead concentration appeared to take on a different value depending upon whether the lead concentration had to build up to that level or whether it started high and dropped to the steady state level. A similar pattern was seen in the steady state NH_3 concentrations.

B. PILOT PLANT OPERATING EFFICIENCY

Essentially, two operations are performed simultaneously by the pilot plant. These are the physical separation of the metallics from the paste materials and the electrochemical reduction of the pastes to metallic lead. The electrochemical reduction of the pastes can be further separated into two distinct steps: leaching and electrowinning.

Metallics Separation

The physical separation of the metallics from the pastes is done exclusively in the leaching column. This is performed by the upward flow of the AAS through a 2.5 cm choke: the velocity of the solution is such that the light paste materials are prevented from entering the choke, while the metallics are heavy enough to fall through the choke.

From the operating runs, it was found that the amount of material reporting to the sinks was governed by three factors: the exact makeup of the feed material, the flow rate of the AAS (and thus its velocity through the choke) and the feed rate of the lead bearing material.

Throughout the runs, variations in the metallics content of the feed material existed not only between different batches of batteries broken for feed, but even to some extent between the individual runs using feed from the same batch of batteries. This can be seen both for individual runs in a set, where no clear relationship was established between "% feed to sinks" and AAS flow rate (Figure 30), as well as for a composite graph of a number of runs where a wide variation in the "% feed to sinks" is shown even at constant AAS flow rates (Figure 38).

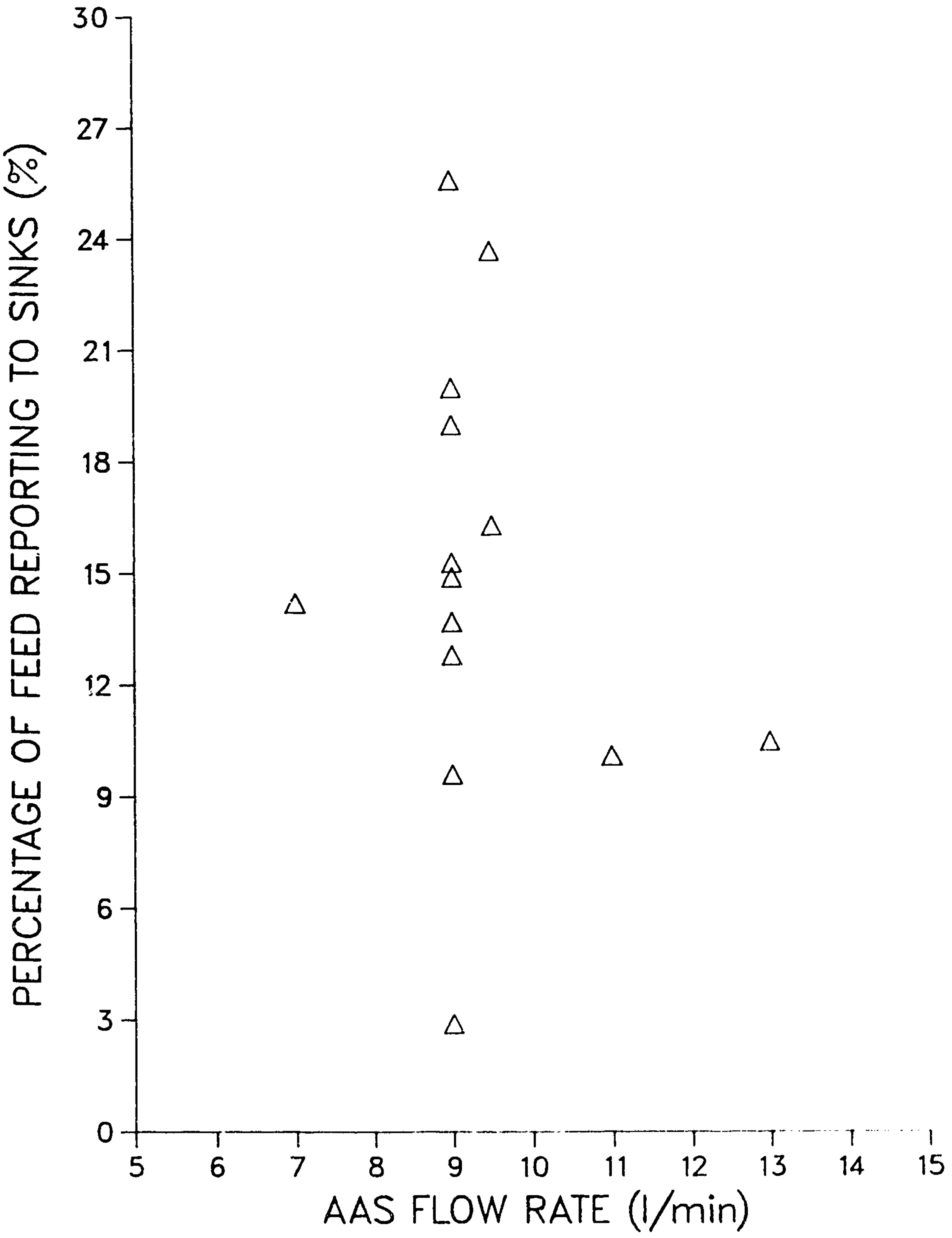
While the effect of AAS flow rate upon the "% feed to sinks" was clouded by variations in the feed material, a very clear relationship was shown in how cleanly the metallics separation was effected at different AAS flow rates (Figure 31).

The final factor is battery fines feed rate. It can be seen from Figure 21 that the higher the fines feed rate, the greater is the "% feed to sinks". As discussed previously, this was likely due to a "clumping" effect allowing, or a "crowding" effect forcing, more of the feed through the choke.

Paste Leaching

In the test results, the leaching efficiency was defined as the amount of feed material dissolved during the run, divided by the amount of feed material available to be dissolved (being the total feed less that reporting to the sinks). Thus, the only "losses" are fines carried over and settled out in the settling tank (or electrowinning tank) and those still held in suspension in the leaching column at

FIGURE 38. METALLICS SEPARATION: AAS FLOW RATE



the end of the run.

Based on the preliminary experiments, it was expected that the factors controlling the leaching would be the NH_3 and $(NH_4)_2SO_4$ concentrations as well as the lead concentration. The NH_3 and $(NH_4)_2SO_4$ levels were demonstrated to control the maximum lead concentrations attainable and the lead concentration itself would determine how much of this capacity remained to dissolve more lead.

The NH_3 and $(NH_4)_2SO_4$ concentrations, in the ranges investigated, showed no direct relationship to leaching efficiency (NH_3, Figures 26 and 39; $(NH_4)_2SO_4$, Figure 40). The lead concentration, however, did prove to be a major factor in the leaching efficiency.

The lead concentration itself was affected by the NH_3 concentration, the current density and the battery fines feed rate; thus, these three factors did affect the leaching through their effect on the lead concentration. The NH_3 concentrations investigated in Run 3 (Figure 23) did not show a clear effect on the steady state lead concentration (Figure 24). On the other hand, a composite graph for all the runs did demonstrate a relationship between the NH_3 concentration and the lead concentration (Figure 41). Considering the minimal effect of higher NH_3 concentrations on lead concentration, however, it is not surprising that this relationship does not significantly affect leaching efficiency.

FIGURE 39. PASTE LEACHING: AMMONIA CONCENTRATION

(@ 50 amps (baffles only), 60 g/min Pb feed)

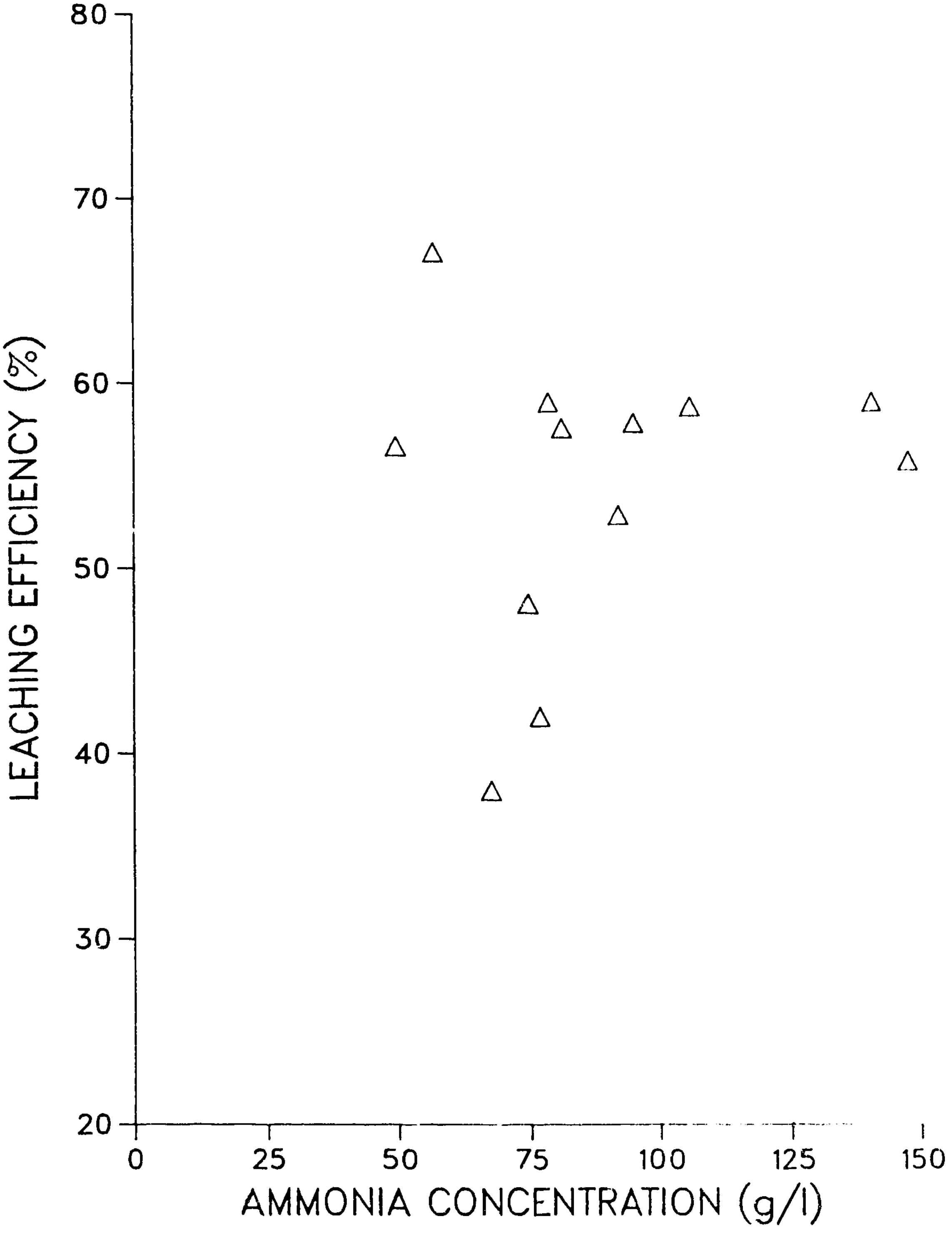


FIGURE 40. LEACHING: SULPHATE CONCENTRATION

(@ 50 amps (baffles only), 60 g/min Pb feed)

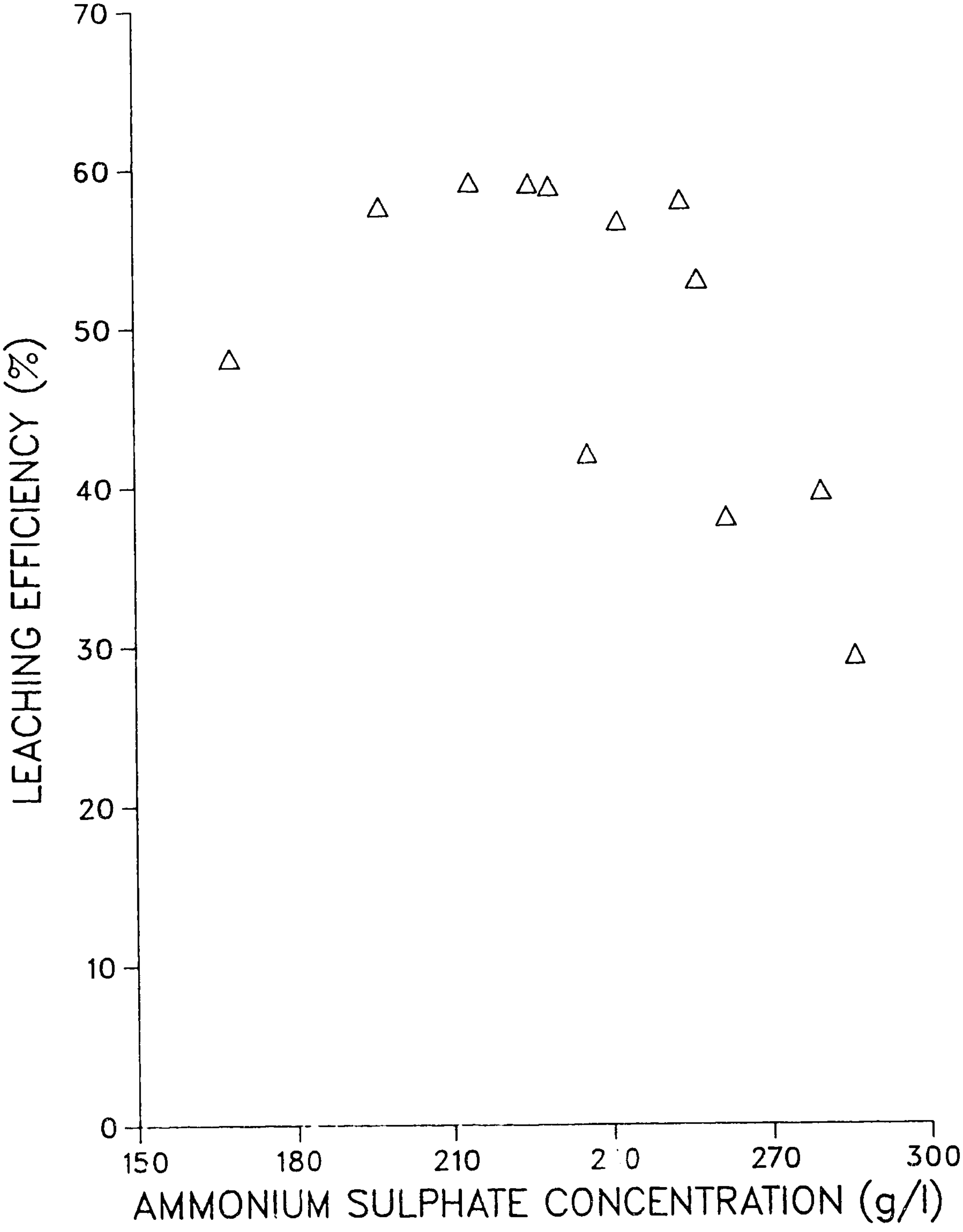
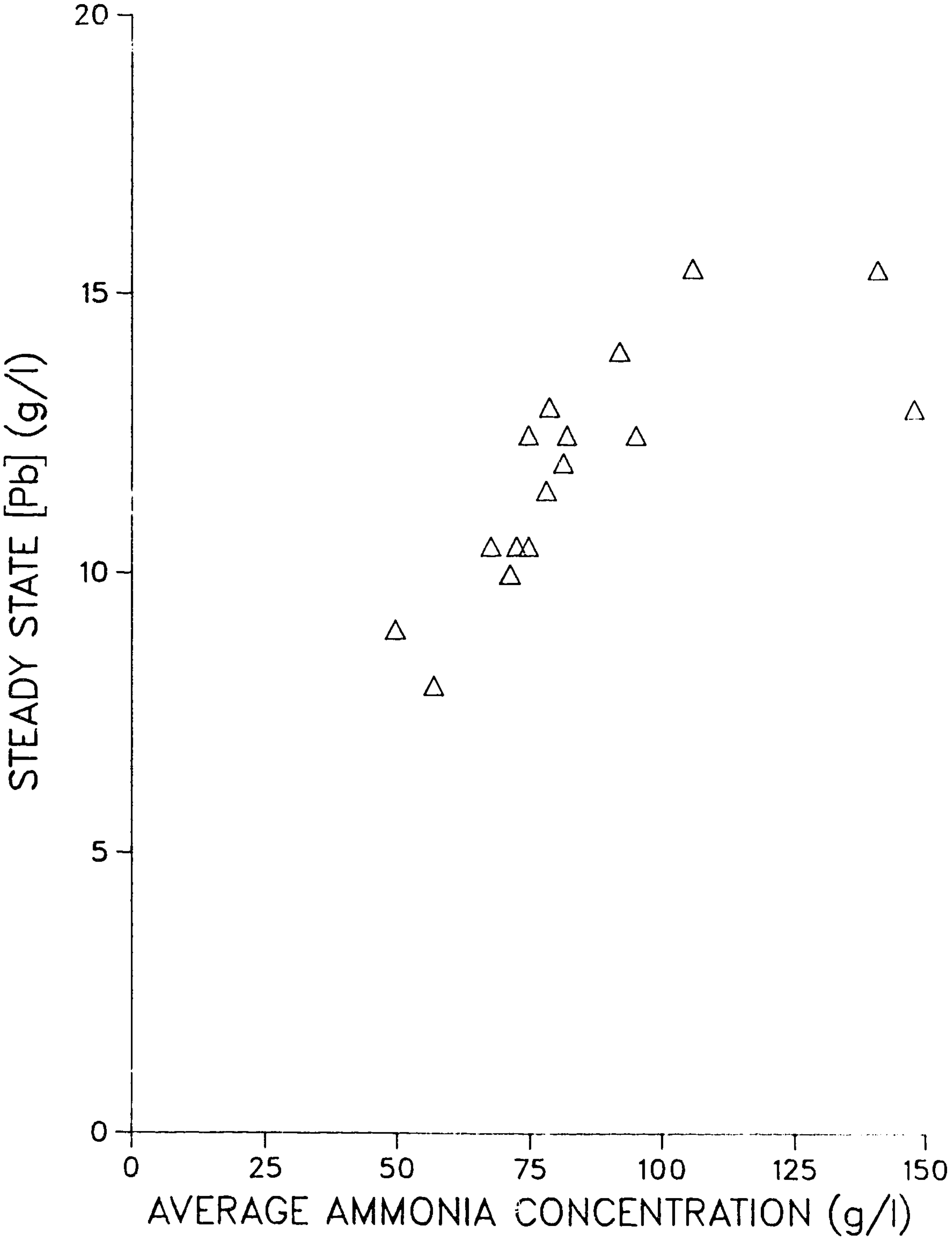


FIGURE 41. PASTE LEACHING: LEAD CONCENTRATION

(@ 50 amps (baffles only), 60 g/min Pb feed)



The lead concentration was greatly affected by both the current density and the fines feed rate. Both of these relationships were strong enough to manifest themselves in the leaching efficiency.

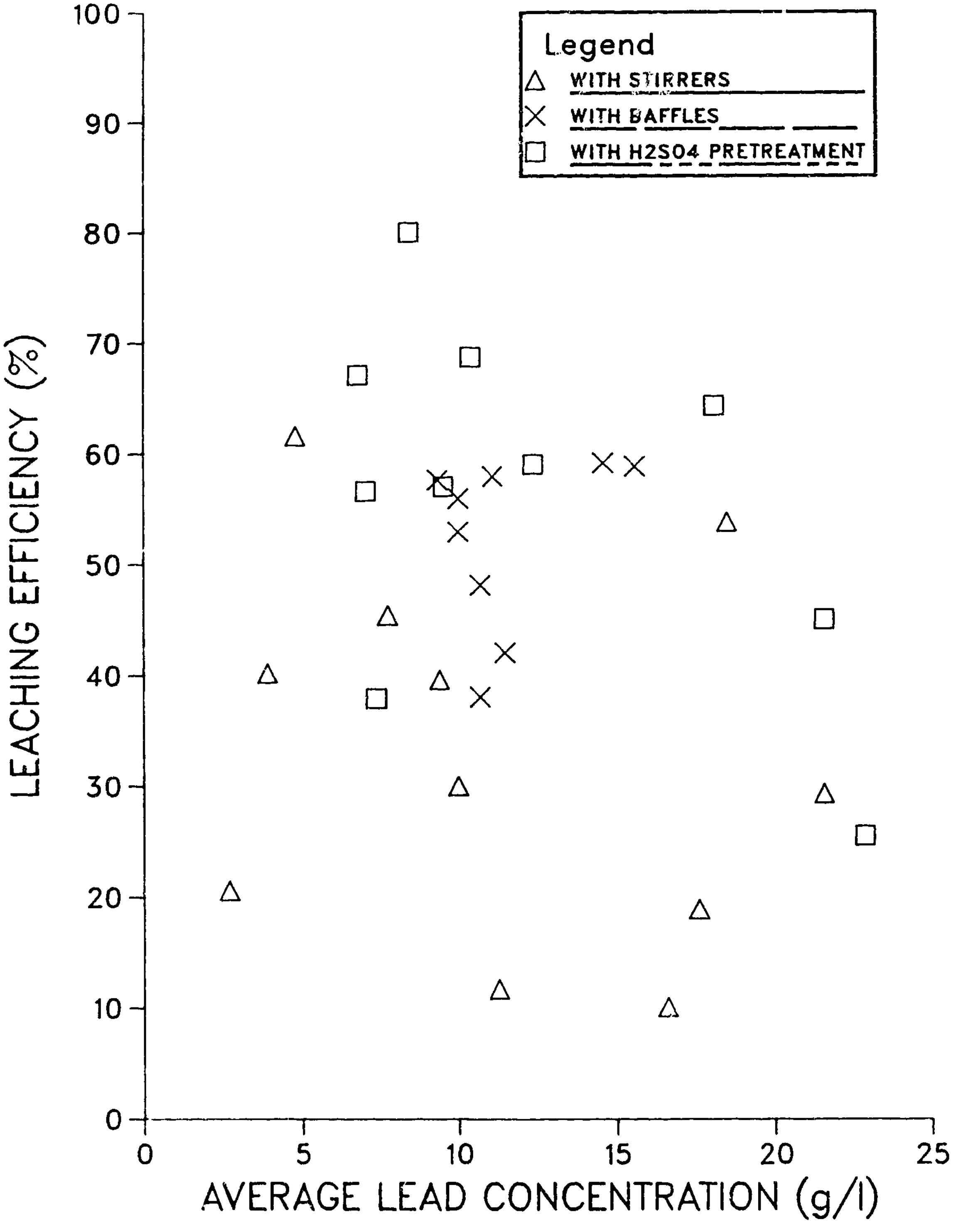
Increased current density reduced the AAS lead concentration (Figure 16), leaving the AAS with greater capacity to dissolve lead. This did result in better leach efficiencies (Figure 17). Because the current density did not affect any other aspect of the leaching except the AAS lead concentration, this leads to the conclusion that the lead concentration is very important in leaching efficiency.

The fines feed rate affected leaching efficiency through two routes. First, an increased feed rate meant more fines exposure to the AAS and thus a higher lead concentration (Figure 18). The higher lead concentration reduces the leaching capacity available to dissolve more lead, yielding a lower leach efficiency. Secondly, a higher fines feed rate results in a higher AAS slurry density. This will tend to float coarser material, resulting in fines being carried over into the settling tank sooner (giving them less opportunity to dissolve). A balance will be reached at any particular feed rate where the undissolved fines will increase the slurry density of the AAS until fines are being floated out of the column at the same rate as those fines which are not dissolving are being fed into the column. The general trend of decreased leach efficiency with increased fines feed rate is apparent in Run 2 (Figure

20). In Run 7, the leaching was operated at only 20% of its usual production rate (i.e., fines feed rate). The highest leach efficiencies, up to 80%, were achieved with this run. Finally, the 50% increase in fines feed rate for Run 9 (as compared to Run 8), resulted in a drop in the leach efficiency from the 50% range (Run 8) to 26% (Run 9). In the composite graph (Figure 42), the amount of scatter in the data tends to hide the relationship between the lead concentration and leach efficiency. If, however, the data for runs with and without baffles are examined separately, the trend is discernable.

There are a number of factors which could account for the scatter in the data which tends to obscure the previously mentioned relationships. Firstly, the samples for lead analysis were taken at the leach column exit. The lead concentration at this point depends upon many things and is not necessarily indicative of the lead content of the AAS returning from electrowinning (at a set AAS flow rate the difference in lead content between the AAS entering and the AAS exiting the leach column will determine the leaching efficiency). In Figure 42 it can be seen that the leach efficiencies were generally higher after stirrers in the electrowinning tank were replaced with baffles. The baffles increased the electrowinning efficiency (as shown later) and would therefore result in a greater difference in the lead concentrations between the entrance and exit of the leach column.

FIGURE 42. PASTE LEACHING: LEACH EFFICIENCY



Differences in the properties of the battery fines feed material can also affect the leaching. A finer ground feed may result in faster $PbSO_4$ dissolution or may result in more material being carried into the settling tank where, once it has settled, it is no longer susceptible to leaching. The $PbSO_4$ content of the feed material may also vary among or within batches of batteries processed for feed. Again, Figure 42 shows that material pretreated with H_2SO_4 generally gave higher leach efficiencies than untreated material (for a given average AAS lead concentration).

Finally, the **Multiple Leaches** in the Preliminary Experiments must be considered. When leaching battery fines in five consecutive batches of fresh AAS, less than 60% of the fines dissolved. If 60% is considered the "target" for leach efficiency, then the leaching system performed quite satisfactorily.

Electrowinning

The important parameters of electrowinning are the energy consumption (kWh/kg Pb recovered) and closely related to it, the current efficiency. As with leaching, the efficiency of electrowinning is dependent upon a number of interrelated factors. These include the current density employed, the lead concentration of the AAS, the agitation (or exposure of fresh electrolyte to the electrode surfaces) and the physical design of the electrowinning system.

The main factor in electrowinning is the current density employed. In the first operating run, current densities from 0.5 amps/sq dm to 20 amps/sq dm were investigated. The highest current efficiency for this investigation was 34.5% at 6.1 amps/sq dm (Figure 15), but the lowest power consumption was 0.6 kWh/kg at 0.5 amps/sq dm (which reflects the low voltage needed to obtain this current). In order for the system to operate at a reasonable level of productivity, the lead must be removed from the AAS at a rate which balances the lead dissolution rate. Thus, the 6 amps/sq dm current density was chosen as it had the highest current efficiency, the second lowest energy consumption and was able to plate lead at a rate comparable to the designed feed rate of the system (at 100% current efficiency the plating capacity at 6 amps/sq dm is approximately 32 g/min).

After optimizing other process parameters, the current density was again investigated in Run 8 (Figure 36). This time current densities of 3.1 to 6.3 amps/sq dm resulted in current efficiencies between 63% and 83% and energy consumptions between 0.5 and 1.0 kWh/kg. These current efficiencies are quite reasonable in comparison to other published results, where over 75% is considered satisfactory.[1]

The lead concentration of the AAS is the second major factor contributing to electrowinning efficiency. The investigation of fines feed rate (and thus lead concentration, Figure 18) shows a clear relationship with current efficiency (Figure 19). Generally, higher current efficiencies and lower energy consumptions were obtained with higher lead concentrations in the AAS. Although there is more scatter in the data when a composite graph is drawn for all the runs, the above mentioned trends can still be seen for both current efficiency (Figure 43 - with baffles) and energy consumption (Figure 44 - with baffles).

The third factor is the physical design of the electrowinning system itself. This includes the electrode spacing and the amount of agitation at the electrode surface. The effect of electrode spacing was investigated in Run 7. Increasing the electrode spacing generally resulted in slightly higher current efficiencies (Figure 33). This is most likely due to less short circuiting (both by the metal scraper used to remove the cathode deposit and by the cathode deposit itself). Energy consumption, however, increased dramatically with increased electrode spacing (Figure 34). This is due to the higher voltage required to overcome the resistance of the longer path through the solution. As explained in Run 7, it is desirable to have as narrow a gap between electrodes as possible to keep the energy consumption to a minimum. There is a limit to how narrow this gap can be set, however, as the nature of the deposit requires it be removed continuously. Enough room is needed between the electrodes to allow this to be done without excessive short circuiting of the electrodes.

FIGURE 43. LEAD CONCENTRATION: CURRENT EFFICIENCY

(@ 3 cm electrode spacing, 60 g/min Pb feed)

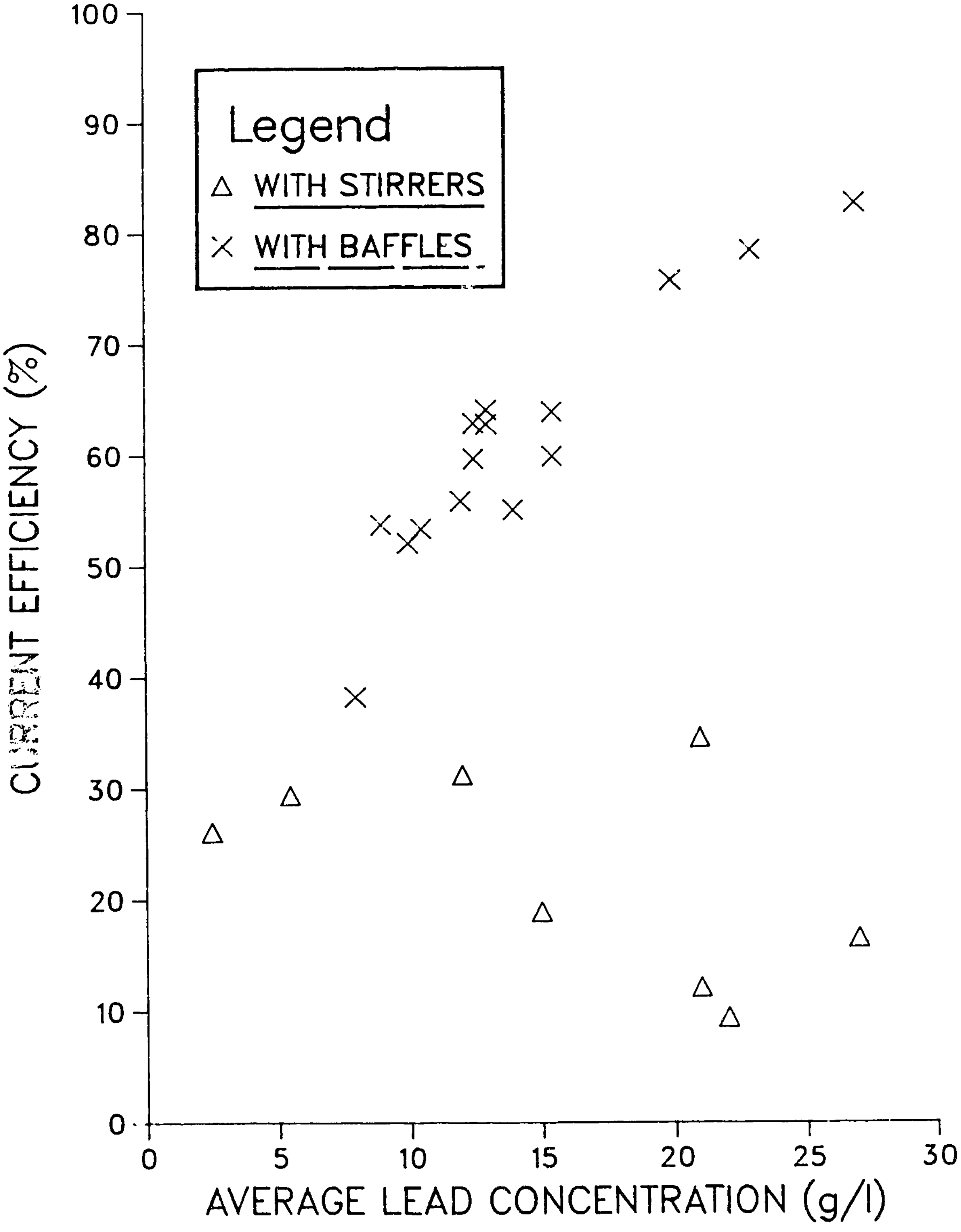
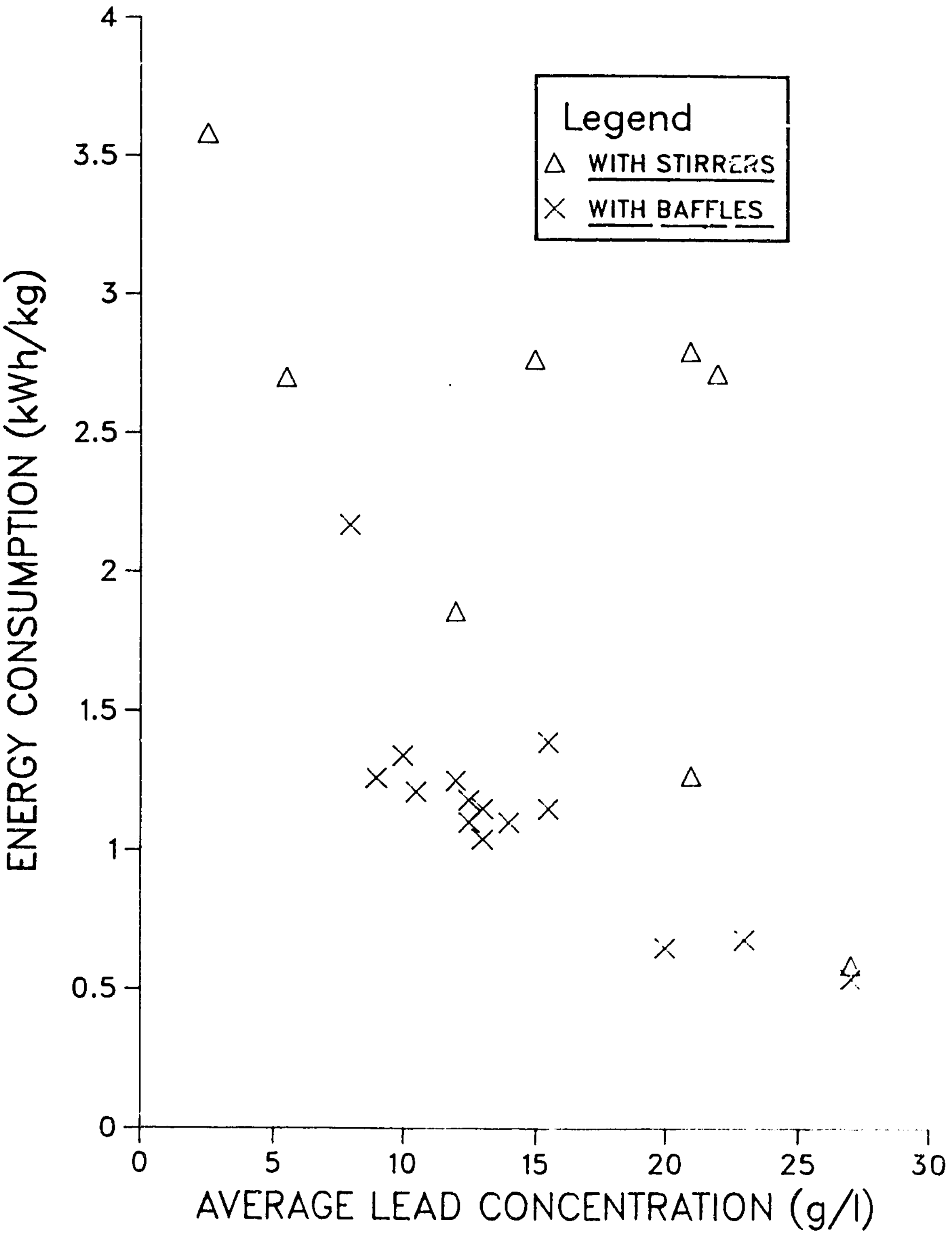


FIGURE 44. LEAD CONCENTRATION: ENERGY CONSUMPTION

(@ 3 cm electrode spacing, 60 g/min Pb feed)



Agitation of the solution was not investigated extensively. Initially, agitation in the electrowinning tank was accomplished with three overhead stirrers which provided a general mixing of the AAS and encouraged, to some extent, AAS flow between the electrodes. For Run 3 and all subsequent runs, the stirrers were replaced by plexiglas "baffles" which blocked the AAS from flowing underneath every second electrode and from flowing over top of the others. In this way the AAS was forced to flow between each pair of electrodes in turn, first upwards, then downwards. These baffles had a very positive effect on the electrowinning efficiency as can be seen both for the current efficiency (Figures 43 and 45) and for the energy consumption (Figures 44 and 46).

Other process variables, including NH_3 concentration (Figure 25), the AAS flow rate (Figure 28) and the addition of various organic agents (Run 5), had no discernable effect on electrowinning. In all cases the cathode deposit was spongy and loosely attached or, at points where agitation was high and current density was low, dendritic and loosely attached to the cathodes. In all cases the deposit was easily removed from the cathodes. Generally, the deposit was attached loosely enough that if it were allowed to build to a thickness beyond approximately 6 mm, the flow of the AAS alone would begin to peel the deposit off of the cathodes. In none of the operating runs was any factor noticed that significantly altered the nature of the cathode deposit.

FIGURE 45. CURRENT DENSITY: CURRENT EFFICIENCY

(@ 3 cm electrode spacing, 60 g/min Pb feed)

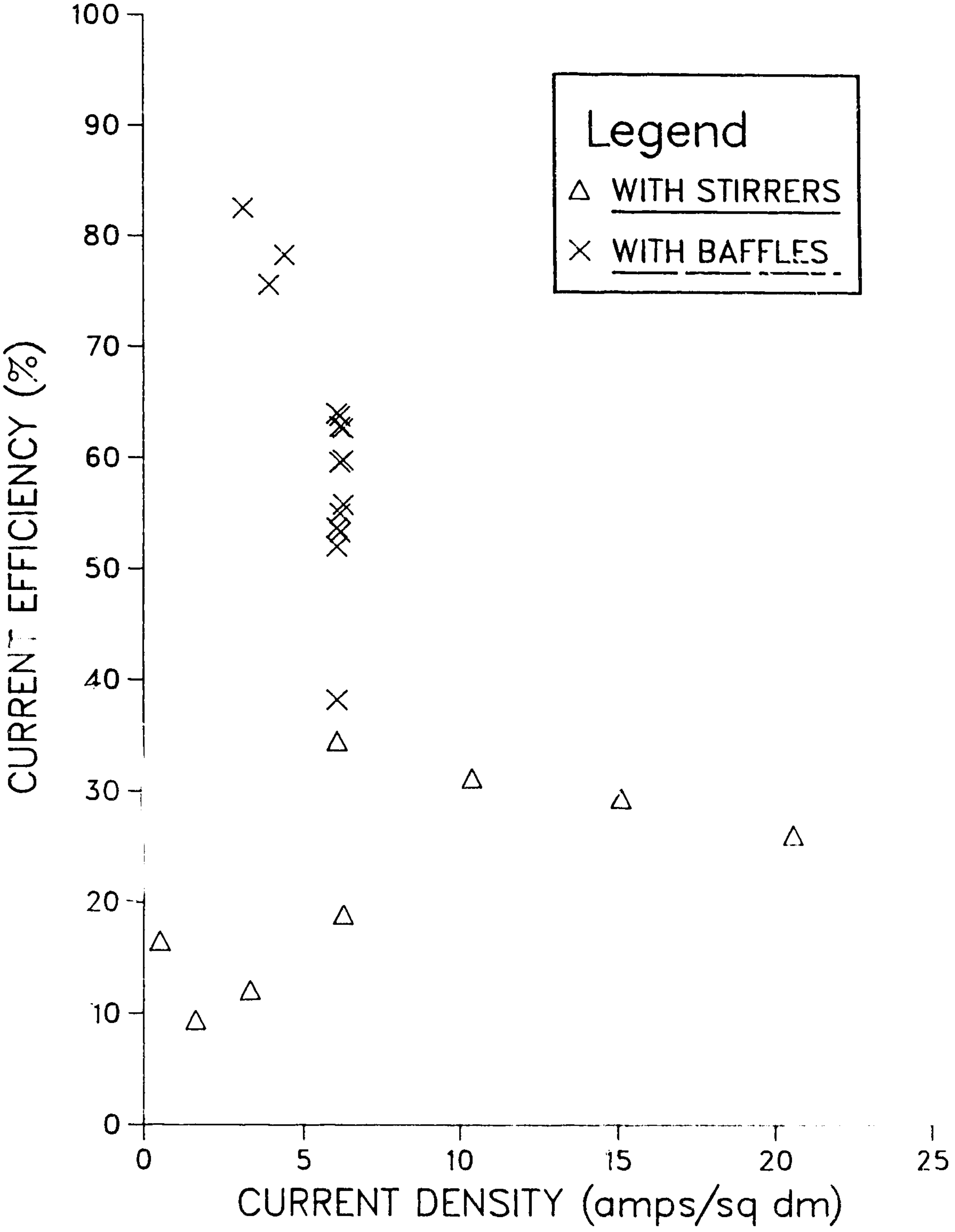
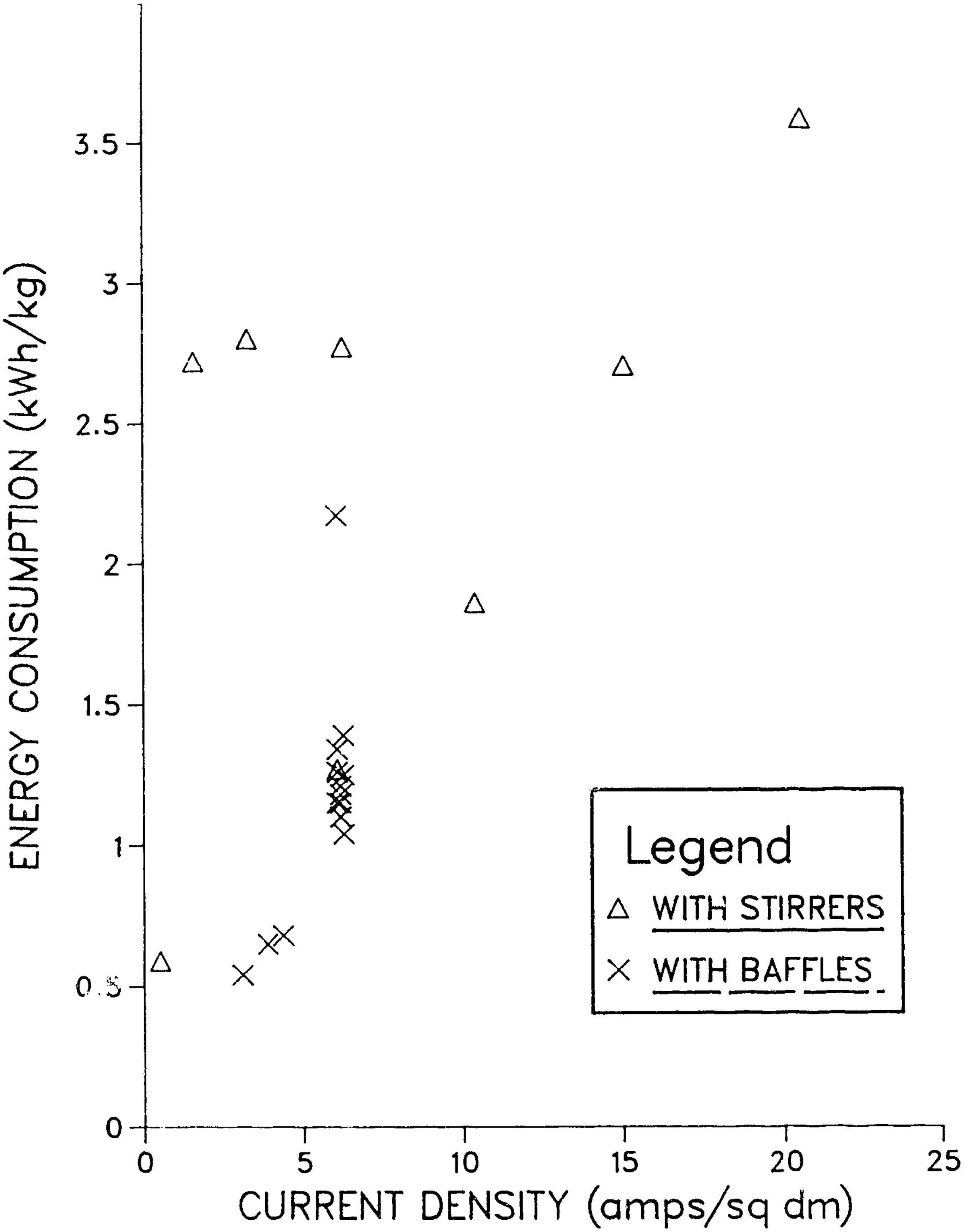


FIGURE 46. CURRENT DENSITY: ENERGY CONSUMPTION
(@ 3 cm electrode spacing, 60 g/min Pb feed)



In contrast to findings by Bratt and Pickering,[130] no appreciable amount of PbO_2 was produced at the anodes. In every run, the amount of anodic PbO_2 produced was too small for it to be recovered and weighed with any accuracy.

C. PILOT PLANT OPTIMIZATION

The factors affecting the pilot plant operation can be classified into two groups: "operating variables" and "plant setup parameters". "Operating variables" refers to those factors which can be easily changed during plant operation (such as electrowinning current, NH_3 feed rate, fines feed rate, etc.) while "plant setup parameters" refers to factors which, while they can be changed, are generally "built in" to the plant design (such as electrode area and configuration, AAS agitation, etc.). The term "operating parameters" refers to the plant operating characteristics which are dependent upon the operating variables and plant setup parameters (these include AAS lead and NH_3 concentrations, current efficiency, etc.).

During the operating runs, the pilot plant demonstrated remarkable stability. When operating, the plant would find a balance between the various operating parameters and would achieve a "steady state" condition. Changing any one operating variable would shift this balance so that the plant would once again achieve a "steady state" condition, but with the operating parameters altered to reflect the change. When evaluating the operating characteristics, it became apparent that these changes usually had a positive effect on some operating parameters while negatively affecting others. Thus, optimizing the plant operating variables involved making a compromise in a tradeoff situation.

Changes to the plant setup parameters involved changes to the plant apparatus or to the process itself and were generally not adjustable during a run (in a commercial operation they would require design changes to the plant itself). These included such things as electrode spacing, the physical setup of the plant (size and arrangement of equipment), the use of H_2SO_4 treatments, etc. Generally, these parameters would be set by constraints other than the operating characteristics of the plant itself (such as size constraints, or accessibility of cathodes, etc.). Changes to these setup parameters generally had the effect of shifting the entire balance of the system in favour of (or to the detriment of) all the operating parameters at once.

The three main "tradeoff" situations recognizable with this pilot plant were between the metallics cleaning efficiency (or separation efficiency) and the leaching efficiency; the productivity of the plant and the separation and leach efficiencies; and, most importantly, between the leaching and electrowinning efficiencies.

The tradeoff between the separation efficiency and leaching efficiency is closely tied to the plant productivity. The AAS flow rate affected only the separation and leach efficiencies. Low AAS flow rates allowed more nonmetallics to enter the sinks trap, lowering the separation efficiency. High AAS flow rates effected a better separation, but also washed fines out of the leach column sooner, resulting in lower leach efficiencies.

Increasing the battery fines feed rate improved the productivity of the plant, but lowered both the separation and leach efficiencies. Higher fines feed rates forced more nonmetallics into the sinks trap, while at the same time increasing the AAS lead concentration and slurry density; both of which served to lower the leaching efficiency.

The tradeoff between the leaching efficiency and the electrowinning efficiency was based on the lead concentration of the AAS. Changes which resulted in higher lead concentrations favoured electrowinning, most likely by reducing the lead ion concentration gradient at the cathode surface. Lower lead concentrations left the AAS with greater leaching capacity and thus, improved leach efficiency.

The operating variables affecting the AAS lead concentration were the NH_3 feed rate, the fines feed rate and the electrowinning current. Higher NH_3 concentrations affected leach efficiency very little, while higher fines feed rates greatly increased the lead concentration, improving electrowinning efficiency to the detriment of leaching efficiency. Higher electrowinning current densities lowered the lead concentration, improving leaching efficiency at the expense of electrowinning efficiency.

The plant "setup" parameters generally shifted all the operating parameters rather than yielding tradeoffs. Improvements were made to most or all of the operating parameters by replacing the electrowinning tank stirrers with baffles, by narrowing the electrode spacing (limited by accessibility of the cathodes for deposit removal) and by H_2SO_4 treatment of the feed material (or settling tank slimes). It is these types of improvements that are of the most value because the positive effect on some operating parameters is not offset by a negative impact on others.

D. UNRESOLVED CONCERNS AND SUGGESTIONS FOR FUTURE WORK

Based upon discussions in the previous section, improvements that can be sought in the mechanical separation are decreasing the amount of lead compounds reporting to the sinks while ensuring that fine metallics are not being carried out of the leach column into the settling tank. In the operating runs, the best results were obtained at low fines feed rates. Thus, to allow for the same capacity while increasing the separation efficiency, a larger leach column would have to be used. The same 2.5 cm choke should be used (if AAS flow rates were to remain unchanged) but a larger top diameter would lower the vertical velocity of the AAS, decreasing the size of material which would wash out.

Using a larger leach column should improve the leach efficiency by allowing more time for dissolution (fines would stay in the column longer due to the lower AAS slurry density and velocity). It may also be useful to try two tanks in series for leaching. The first would separate the bulk of the metallics and start paste dissolution, the second would be larger to separate the finer metallics and provide a longer residence time for paste dissolution.

However the leach system is designed, as it operates it will achieve a balance; fines will accumulate in the system until the slurry density of the AAS is such that pastes are "floated" out at a rate equal to the rate at which feed material which is not dissolving is entering the leach system. Even if all the PbO and $PbSO_4$ dissolves in the leach system, this balance will be achieved with the PbO_2 present in the feed.

The final improvement needed in the leach system is the way the H_2SO_4 treatments are performed. The hotplate used to heat the beakers of feed material did not hold the slurries at a high enough temperature. The PbO_2 to $PbSO_4$ conversion was more effective at the bottoms of the beakers (evidenced by the colour change from brown to grey), but generally no colour change was noticed at the tops of the beakers where the temperature was as much as 20°C colder. Thus, a proper facility for heating the H_2SO_4 slurry (possibly a drying oven) where higher temperatures could be achieved with more uniform temperature throughout the slurry could dramatically increase the effectiveness of the H_2SO_4 treatment. After these improvements are implemented, runs should be set up to determine the best sequence for achieving optimum recovery.

That is, whether the feed material should be pretreated prior to leaching or if it would be more efficient to feed battery fines directly into the leaching, then treat the settling tank slimes prior to recycling them to the leach column.

It would be hoped that improvements to the leaching system would result in higher lead concentrations in the AAS flowing into electrowinning; this would help to improve the electrowinning efficiency.

Regarding the electrowinning system itself, the best chance for improving the efficiency would be to improve agitation in the tank. Using the same electrode design, this could be accomplished by circulating the AAS at a higher rate using extra pumps. It may also be worthwhile to try increasing the number of electrodes so that the current density could be lowered without sacrificing plating capacity. (Note that if the leach tank is enlarged and more electrodes are used in electrowinning, this is simply a scale-up of the design, equivalent to decreasing the fines feed rate and electrowinning current density with the existing setup.) If the electrowinning system itself is to be changed, two different systems which would be worthwhile investigating are the use of rotating cathodes or the elimination of electrowinning entirely by recovering the lead using hydrogen reduction.

When reviewing the data from the operating runs, one striking problem is the high NH_3 consumption. This ranges from a low of 0.64 kg/kg Pb to a high of 12 kg/kg Pb. Theoretically, only 0.16 kg of NH_3 is needed per kg Pb produced. The main reason for this high consumption is evaporation losses from the settling and electrowinning tanks. Although the evaporation rate is dependent upon the NH_3 concentration, even at low concentrations the amount of evaporation is significant (Figure 27).

The only way to prevent these losses is to seal the entire system. Although the leaching column and settling tank can easily be sealed, the electrowinning tank poses a problem. During the operating runs, constant access to the cathodes was needed to allow for removal of the cathode deposit. Thus, in order to seal the electrowinning tank, some method of automatically scraping the cathodes would have to be devised. One way this could be accomplished would be to design the tank and electrodes such that the AAS flow itself would remove the deposit (as previously mentioned, the AAS flow did peel off some of the deposit when the thickness was allowed to build up). This would be aided by a higher AAS flow rate, if it were employed to improve agitation in the electrowinning tank. A settling section would then have to be designed into the electrowinning tank to hold the cathode deposit until the end of each run.

The final concern is the recovery of $(NH_4)_2SO_4$ which is produced by the neutralization of H_2SO_4 and the reduction of $PbSO_4$. Removal of $(NH_4)_2SO_4$ from the AAS used in the pilot plant operating runs was disregarded as it crystallized out (and was left behind) in the storage containers between runs. The recovery method employed and the resulting lead concentration of the $(NH_4)_2SO_4$ must be investigated to ensure the $(NH_4)_2SO_4$ would be suitable for use as fertilizer.

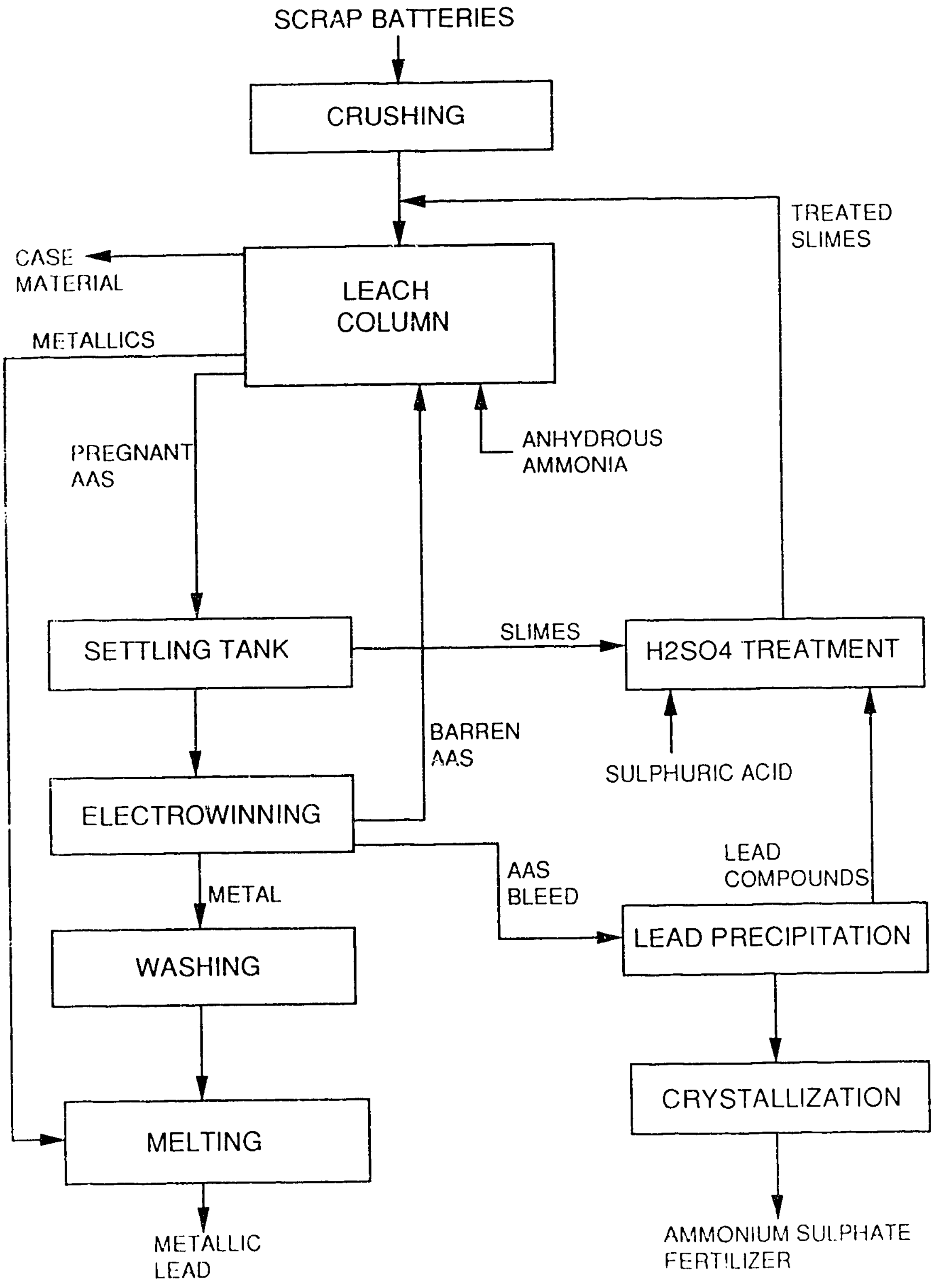
VIII. CONCLUSION

This study developed a pilot plant and process for recovering the lead contained in scrap lead-acid batteries. The process uses an ammoniacal ammonium sulphate solution to physically separate the metallics contained in crushed battery scrap while simultaneously electrochemically recovering metallic lead from the lead compounds. The process is summarized in the final flowsheet, Figure 47.

In operating the pilot plant, changes to the operating variables yielded tradeoffs in the various operating efficiencies. The best compromise found for the operating variables was a battery fines feed rate of 60 g/min (of paste material), an AAS flow rate of 9 l/min, and a low NH_3 feed rate (approximately 20 g/min yielding an NH_3 concentration of 75 to 100 g/l). This yielded a steady state AAS lead concentration of approximately 20 g/l. The electrowinning was operated with 10 cathodes on 3 cm spacings at 3.9 amps/sq dm (30 amps total) which gave a current efficiency of approximately 76% with an energy consumption of 0.65 kWh/kg Pb.

Changes to the design and setup of the pilot plant itself (previously referred to as "plant setup parameters") tended to improve the overall performance of the plant without the tradeoffs encountered in changes to the "operating variables". It was felt further investigations into these design changes would be justified.

FIGURE 47. FINAL PROCESS FLOWSHEET



Overall, the pilot plant and the AAS process proved to be an effective treatment route for scrap battery material. The environmental problems currently facing battery recyclers were solved by this process; being a wet process, no lead dust is produced and undesirable properties of batteries from a recycling perspective (such as the acid electrolyte and sulphates in the paste material) are turned to advantages through the coproduction of $(NH_4)_2SO_4$ fertilizer.

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X. APPENDIX I. RESULTS OF PRELIMINARY EXPERIMENTS

TABLE 1 CHARACTERIZATION OF SCRAP BATTERIES

Component weights (kg) for:

BRAND	VOLTAGE	WET	DRAINED	CASING	SEPARATORS	METALLICS	FINES
Unknown	6	15.11	11.82	2.50 (HR)	0.68	2.27	6.37
Firestone	12	17.04	13.41	1.14 (P)	0.91	3.18	8.18
Motorcraft	12	21.36	18.86	0.91 (P)	1.14	3.18	13.63
Autopar	12	16.48	11.82	0.91 (P)	0.80	3.30	6.81
Mopar	12	18.41	17.04	3.18 (HR)	1.25	2.73	9.88

HR=Hard Rubber

P=Polypropylene

TABLE 2: SIEVE ANALYSIS OF BATTERY FINES

SIEVE MESH #	% RETAINED
6	0.2
8	0.5
10	0.5
14	1.1
20	2.1
28	0.9
35	0.3
48	2.7
65	4.6
100	6.1
150	15.1
200	10.2
minus 200	55.7

TABLE 3: SOLUBILITY OF LEAD SULPHATE IN AAS

Pb concentration (g/l) at sample times:

AAS COMPOSITION*	1	2	5	10	15	20 minutes
0:300:0	0.4	0.3	0.2	0.1	0.1	0.1
100:200:0	1.3	1.4	1.5	1.7	2.0	1.7
200:100:0	0.9	1.6	1.9	2.0	2.0	2.0
300:0:0	1.0	2.6	4.4	4.4	4.4	4.4
50:250:25	2.3	1.8	0.8	0.7	0.6	0.6
150:150:25	4.0	4.8	4.2	4.3	4.0	3.9
250:50:25	-	22.1	21.6	17.6	16.2	14.0
0:300:50	0.7	0.7	0.6	0.6	0.5	0.4
50:250:50	-	3.8	2.9	2.5	2.1	2.1
150:150:50	-	19.2	17.8	13.7	12.4	11.4
250:50:50	53.7	-	73.2	56.1	47.6	41.4

TABLE 3: continued

AAS COMPOSITION*	Pb concentration (g/l) at sample times: 1	2	5	10	15	20 minutes
50:250:100	-	13.2	7.2	5.0	4.8	4.4
150:150:100	36.0	45.2	50.0	28.3	24.5	20.6
250:50:100	153	154	154	151	133	138
0:300:150	3.6	3.0	3.4	1.4	-	1.7
50:150:150	26.4	25.5	21.8	-	9.0	7.6
150:150:150:	86.3	90.8	98.6	74.2	72.4	68.2
250:50:150	170	176	175	156	136	122
50:250:200	38.2	41.0	29.1	-	15.1	13.6
150:150:200	69.4	86.7	90.6	93.0	80 0	71.8
250:50:200	154	164	169	163	144	127
0:300:250	6.6	10.2	-	-	10.0	-

*AAS Composition: [ml NH_4OH]:[ml H_2O]:[g $(NH_4)_2SO_4$]

TABLE 4: SULPHURIC ACID PRETREATMENT OF BATTERY FINES

RUNS

1. Control - no H_2SO_4 treatment.
2. 10 minute treatment in 271 g/l H_2SO_4.
3. 10 minute treatment in 706 g/l H_2SO_4.
4. 12 hour treatment in 271 g/l H_2SO_4.
5. 5 hour treatment in 706 g/l H_2SO_4.

RUN	[Pb] (g/l)	AAS VOL.(ml)	DISSOLVED Pb (g)	$PbSO_4$ CONTENT (%)
1	21.8	352	7.67	56.1
2	22.8	359	8.18	59.9
3	23.8	372	8.84	64.7
4	23.0	377	8.69	63.6
5	23.0	351	8.05	59.0

TABLE 5: SOLUBILITY OF PRETREATED BATTERY FINES IN AAS

	Pb concentration (g/l) at various times:					
AAS COMPOSITION*	1	2	5	10	15	20 minutes
100:200:125	41.4	36.1	33.4	28.4	26.6	24.1
125:175:125	58.1	56.0	53.4	60.5	51.8	41.2
150:150:125	58.0	77.2	77.4	71.4	79.2	
100:200:150	48.8	41.4	39.2	36.6	39.4	-
125:175:150	53.2	77.3	74.0	59.1	64.1	78.6
150:150:150	64.0	78.9	80.7	98.9	98.2	57.2**
175:125:150	53.8	57.6	69.6	63.6	67.0	-
100:200:175	54.6	54.3	52.6	47.6	43.5	45.0
125:175:175	52.1	71.4	79.2	82.4	82.6	64.4
150:150:175	60.9	84.7	76.5	93.2	82.5	54.4**

*AAS Composition: [ml NH_4OH]:[ml H_2O]:[g $(NH_4)_2SO_4$]

**These samples were taken at 15 minutes and allowed to clarify for 20 minutes before analysis.

TABLE 6: ELECTROWINNING CURRENT DENSITY

VOLTAGE	1.5 cm.	1.5 cm.	2.5 cm.	3.5 cm.	4.5 cm.	5.5 cm	6.5 cm.
	Current density (amps/sq dm) at electrode spacing of:						
1.3	0.1	0.2	0.5	0.6	0.2	0.3	0.5
1.5	1.4	1.8	1.4	1.3	1.1	0.7	1.0
1.7	2.6	3.7	2.5	2.2	2.0	1.3	1.6
1.9	3.9	5.3	3.4	3.2	3.1	1.8	2.3
2.0	4.6	6.1	3.9	3.6	3.6	2.0	2.6
2.5	9.1	11.2	7.1	5.8	5.8	3.6	4.0
3.0	14.3	17.6	11.1	9.1	8.4	5.5	5.8
3.5	18.3	-	15.0	12.6	11.4	7.5	8.5
4.0	23.6	30.2	18.8	15.5	15.5	9.8	10.8
4.5	22.9	-	22.6	18.9	20.1	11.3	13.2
5.0	30.1	45.9	26.3	22.9	24.5	13.3	15.6
	Pb concentrations (g/l):						
1.3	26.4	64.3	40.1	47.8	77.0	20.3	35.6
2.0	24.2	60.9	27.9	40.6	-	19.2	37.5
5.0	15.6	-	-	31.0	-	14.3	32.4

TABLE 7: RESULTS OF ELECTROWINNING TRIALS

RUN	I	CDW	ADW	CD	CE	[Pb]	[Pb]'
1	20.2	-	0.7	28.0		13.9	11.3
2	22.1	25.6	0	28.7	60.0	31.9	1.4
3	9.6	6.1	2.0	12.9	32.9	38.1	13.2
4	11.9	18.3	1.1	16.5	79.4	38.1	5.9
5	4.7	6.1	1.7	6.9	66.7	31.4	17.1
6	5.5	7.8	1.7	8.4	72.9	26.4	9.9
7	2.3	2.2	6.7	3.3	47.9	14.6	13.9
8	2.0	2.5	2.7	2.8	63.8	15.0	14.4

I= average amperage

CDW= cathodic Pb recovered (after melting) (g)

ADW= anodic PbO, recovered (g)

CD= current density (amps/sq dm)

CE= current efficiency (%)

[Pb]= initial Pb concentration (g/l)

[Pb]'= final Pb concentration (g/l)

XI. APPENDIX II. INITIAL DESIGN CALCULATIONS

LEACH TANK

Fines Feed Rate

Basis: A plant processing 1000 batteries per day, operating 20 hours per day.

(1000 bat/day x 9.54 kg fines/bat) / (20 hr/day x 60 min/hr) = 7.95 kg fines/min.

For a bench scale pilot plant on 1/100 scale, processing rate would be 80 g/min. With fines containing 90% lead, production would be 72 g/min of metallic lead.

AAS Flow Rate

Assume the AAS [Pb] is 50 g/l from leaching, with 60% extraction in electrowinning, the return to leaching would be 20 g/l.

(72 g/min feed) / (30 g/l dissolved) = 2.4 l/min AAS flow rate required.

AAS Exit Velocity

From Stokes' law:

Settling velocity of fines

$v = (d^2 \times$ [illegible] $dl) \times g) / (18 \times u)$

where:

ds = density of the solids = 6 g/cm^3 ($PbSO_4$)

dl = density of the liquid = 1.2 g/cm^3 (measured)

g = gravitational acceleration = 981 cm/s^2

u = viscosity of the liquid = 0.012 g/cm-s (estimated)

d = particle diameter (cm)

v = particle velocity through liquid (cm/s)

therefore: $v = (d^2 \times (6 - 1.2) \times 981) / (18 \times 0.012)$

$v = 21800 \times d^2$

for a 200 mesh particle size, i.e., 74 micron diameter $v = 21800 \times (0.0074)^2 = 1.19$ cm/s. If the AAS velocity is set at 10% of this value, say 0.1 cm/s, then particles smaller than:

$d = \text{sq rt } (0.1 / 21800) = 0.00214$ cm or 21 micron

would be entrained in the AAS and carried out of the leach tank.

Tank Exit Area

$(2400\ cm^3/min) / (60\ s/min \times 0.1\ cm/s) = 400\ cm^2$

Tank Volume

Assume a 5 min residence time for the AAS

2.4 l/min x 5 min = 12 l

ELECTROWINNING

Current Required

Electrowinning must plate 72 g/min of lead.

(72 g/min x 2 eq/mol x 96485 C/eq) / (207.2 g/mol x 60 s/min) = 1117 amps

at a target current efficiency of 90%:

1117 / .90 = 1241 amps are required.

Electrodes

At a current density of 15 amp/sq dm:

1241 amps / 15 amps/sq dm = 82.7 sq dm of electrode area is needed.

If 10 electrodes are used , each must have a surface area of 827 cm^2.

If electrodes are made rectangular, with a width 1.5 times the height, the electrode dimensions would be:

height = sq rt (827 / 1.5) = 23 cm

width = 1.5 x 23 = 35 cm

Power Required

From Figure 3, at 15 amps/sq dm the voltage required would be approximately 3.5 V/cell.

With 10 electrodes in series, electrowinning would require 124 amps at 35 volts. This is within the range typical of welders, so should allow the use of a DC welder as a power source.

XII. APPENDIX III. RESULTS OF OPERATING RUNS

ABBREVIATIONS USED IN APPENDIX II

V: Average voltage for the run.

I: Average amperage for the run.

[A]: Average NH_3 concentration (g/l).

[AS]: Average $(NH_4)_2SO_4$ concentration (g/l).

CDW: Weight of cathodic Pb recovered (after melting) (g).

CD: Current density (amps/sq dm).

CE: Current efficiency (%).

EC: Energy consumption (kWh/kg cathodic Pb).

[Pb]: Pb concentration at steady state operation (g/l).

AC: NH_3 consumption (kg NH_3/kg cathodic Pb).

Material Balance

$$Pb + FEED = Pb' + CL + SINKS + SLIMES$$

Pb: Initial Pb content of AAS (expressed as $PbSO_4$).

FEED: Total weight of battery fines fed during run.

Pb': Final Pb content of AAS (expressed as $PbSO_4$).

CL: Weight of cathodic Pb (expressed as $PbSO_4$).

SINKS: Total weight of sinks recovered (after drying).

SLIMES: Total weight of material in suspension in the AAS and recovered in the settling tank.

LE: Leach efficiency (LE=(Pb'-Pb+CL)/(FEED-SINKS)).

S%: Percentage of feed recovered as leach column sinks.

MCE: Metal cleaning efficiency (MCE=weight of melted sinks/weight of dried sinks).

RUN 1

(9 cathodes)

RUN	V	I	[A]	[AS]	CDW	CD	CE	EC	[Pb]	AC
1	3.4	4.0	87.4	306	46	0.5	16.5	0.59	27	-
2	8.9	13.0	72.5	305	85	1.6	9.4	2.72	22	-
3	11.8	26.6	62.8	283	224	3.3	12.1	2.80	21	-
4	15.2	50.1	77.5	286	1201	6.1	34.5	1.27	21	-
5	20.2	84.9	104.8	302	1841	10.4	31.2	1.86	12	-
6	27.6	123.4	114.8	306	2523	15.1	29.4	2.70	5.5	-
7	32.5	168.2	91.8	-	3051	20.6	26.1	3.58	2.5	-

RUN	Pb	FEED	Pb′	CL	SINKS*	SLIMES	LE	S% *	MCE
1	2000	6000	4607	67	1026	2300	53.8	17.1	-
2	4687	6000	4122	124	1026	5415	0	17.1	-
3	3851	6000	3924	328	1026	4573	8.1	17.1	-
4	4201	6000	3902	1758	1026	3515	29.3	17.1	-
5	4466	6000	2276	2694	1026	4470	10.1	17.1	-
6	2495	6000	1061	3693	1026	2715	45.4	17.1	-
7	1906	6000	503	4466	1026	1911	61.6	17.1	-

* For these runs the sinks were combined for drying so the SINKS and S% values are averages

RUN 2

(9 cathodes)

RUN	V	I	[A]	[AS]	CDW	CD	CE	EC	[Pb]	AC
10	18.7	50.5	73.3	306	393	6.2	11.2	4.80	2.5	-
25	18.6	50.7	75.3	298	597	6.2	16.9	3.15	6.0	-
50	18.2	51.5	65.9	280	676	6.3	18.9	2.77	15	-
75	16.2	56.2	55.9	277	915	6.9	23.4	1.99	12	-
100	16.2	51.0	57.4	278	642	6.2	24.1	2.57	15	-
150	16.0	50.5	78.4	256	1162	6.2	33.1	1.39	21	6.9

RUN	Pb	FEED	Pb′	CL	SINKS	SLIMES	LE	S%	MCE *
10	645	1200	465	393	165	822	20.6	13.7	73.1
25	512	3000	955	597	412	1548	40.2	13.7	73.1
50	1030	6000	2378	676	895	3081	39.6	14.9	73.1
75	2129	9000	2055	915	1802	6357	11.7	20.0	73.1
100	997	9000	2543	642	1712	5100	30.0	19.0	73.1
150	2269	18000	3641	1162	4599	10867	18.9	25.6	63.9

* The sinks from runs "10" through "100" were melted together, therefore the value for the MCE for these runs are averages.

RUN 3

RUN	V	I	[A]	[AS]	CDW	CD	CE	EC	[Pb]	AC
16.8	24.9	50.7	67.6	262	2088	6.2	53.3	1.21	10.5	0.97
21.0	26.6	51.0	95.1	254	2475	6.2	62.8	1.10	12.5	1.02
118.5	24.9	50.7	92.1	257	2156	6.2	55.0	1.10	14.0	6.60
246	28.4	49.9	148.0	105	2466	6.1	64.0	1.15	13.0	12.0

RUN	Pb	FEED	Pb'	CL	SINKS*	SLIMES	LE	S% *	MCE
16.8	2488	7200	1820	3056	925	3887	38.0	12.8	-
21.0	2269	7200	2278	3622	925	2644	57.9	12.8	-
118.5	1921	7200	2086	3156	925	2954	52.9	12.8	-
246	2122	7200	2022	3609	925	2766	55.9	12.8	-

* For these runs the sinks were combined for drying so the SINKS and S% values are averages.

RUN 4

RUN	V	I	[A]	[AS]	CDW	CD	CE	EC	[Pb]	AC
7	32.1	51.5	141	214	2379	6.3	59.8	1.30	15.5	0.96
9	28.3	50.4	106	229	2488	6.2	63.8	1.15	15.5	0.64
11	27.1	51.2	81.3	197	2211	6.3	55.8	1.25	12.0	5.65
13	27.3	50.9	74.7	168	2348	6.2	59.6	1.18	12.5	1.06

RUN	Pb	FEED	Pb'	CL	SINKS	SLIMES	LE	S%	MCE
7	2305	7200	2470	3482	1026	2527	59.1	14.2	47.8
9	2671	7200	2616	3642	1103	2510	58.8	15.3	58.5
11	1500	7200	1994	3236	730	2740	57.6	10.1	65.3
13	2397	7200	2058	3437	755	3347	48.1	10.5	75.8

RUN 5

RUN	V	I	[A]	[AS]	CDW	CD	CE	EC	[Pb]	AC
Sugar 100 ppm	30.5	49.2	82.0	-	-	-	-	-	12.5	-
Sugar 1 gpl	28.3	49.6	78.1	-	-	-	-	-	11.5	-
Polyhall 361	26.5	50.3	74.7	-	-	-	-	-	10.5	-
S-3732	25.2	50.5	72.4	-	-	-	-	-	10.5	-
Separan	23.8	50.6	71.2	-	-	-	-	-	10.0	-
Avg.	26.9	50.0	76.9	236	2515	6.1	52.0	1.34	10.0	1.62

RUN	Pb	FEED	Pb'	CL	SINKS	SLIMES	LE	S%	MCE
Overall	2433	9000	1921	3681	1465	4366	42.0	16.3	67.2

RUN 6

RUN	V	I	[A]	[AS]	CDW	CD	CE	EC	[Pb]	AC
Slimes	27.2	50.3	58.9	226	1857	6.2	47.8	1.47	9.0	1.59
Feed	26.2	50.0	49.7	242	2075	6.1	53.7	1.26	9.0	2.30

RUN	Pb	FEED	Pb′	CL	SINKS*	SLIMES	LE	S% *	MCE **
Slimes	1701	7200	1564	2718	878	3741	40.8	12.2	48.7
Feed	1152	7200	1582	3037	1080	2653	56.6	15	48.7

* The value of SINKS for the "Feed" run is estimated as is the S%. The values of SINKS and S% for the "Slimes" run has been calculated from this value.

** For these runs the dried sinks were melted together so the MCE values are averages.

RUN 7

RUN	V	I	[A]	[AS]	CDW	CD	CE	EC	[Pb]	AC
1	4.2	49.4	93.3	218	143	6.1	37.4	1.45	12	23.6
2	5.8	50.1	67.5	222	156	6.1	40.3	1.86	10	23.6
3	6.4	50.1	56.9	234	148	6.1	38.2	2.17	8	23.6
5	7.8	50.1	60.7	228	156	6.1	40.3	2.50	7.5	23.6
7	9.5	49.5	77.5	219	166	6.1	43.4	2.83	10	23.6

RUN	Pb	FEED	Pb′	CL	SINKS*	SLIMES	LE	S% *	MCE **
1	1793	720	2031	209	69	204	68.7	9.6	63.2
2	1390	720	1683	228	69	130	80.0	9.6	63.2
3	1134	720	1354	217	69	214	67.1	9.6	63.2
5	1317	720	1336	228	69	404	37.9	9.6	63.2
7	1665	720	1793	243	69	280	57.0	9.6	63.2

* For these runs the sinks were combined for drying so the SINKS and S% values are averages.

** For these runs the dried sinks were melted together so the MCE values are averages

RUN 8

RUN	V	I	[A]	[AS]	CDW	CD	CE	EC	[Pb]	AC
1	17.2	25.0	80.7	281	1594	3.1	82.5	0.54	27	3.42
2	20.6	35.5	85.7	257	2148	4.4	78.3	0.68	23	3.42
3	25.3	51.3	78.7	225	2488	6.3	62.7	1.04	13	3.42

RUN	Pb	FEED	Pb′	CL	SINKS*	SLIMES	LE	S% *	MCE **
1	3696	7200	4510	2333	206	3847	45.0	2.9	41.9
2	2488	7200	3842	3144	206	2496	64.3	2.9	41.9
3	1866	7200	2350	3642	206	2868	59.0	2.9	41.9

* For these runs the sinks were combined for drying so the SINKS and S% values are averages.

** For these runs the dried sinks were melted together so the MCE values are averages.

RUN 9

RUN	V	I	[A]	[AS]	CDW	CD	CE	EC	[Pb]	AC
Only	18.9	31.6	74.8	307	1848	3.9	75.6	0.65	20	1.35

RUN	Pb	FEED	Pb′	CL	SINKS	SLIMES	LE	S%	MCE
Only	4482	12500	3879	2705	4260	6138	25.5	34.1	90.6