

A STUDY OF BY-PRODUCT RECOVERY FROM SPENT
IRON OXIDE GAS PURIFYING MATERIAL

by

SIGMUND CAESAR SCHWARZ

A THESIS

submitted to the

OREGON STATE AGRICULTURAL COLLEGE

in partial fulfillment of
the requirements for the
degree of

CHEMICAL ENGINEER

June 1936

APPROVED:

+82 Bdg.

[REDACTED]

Professor of Chemical Engineering.

In Charge of Major

est. 10.30

[REDACTED]

Chairman of School Graduate Committee.

g. Author

[REDACTED]

Chairman of College Graduate Council.

22001 36

TABLE OF CONTENTS

Approval	Page ii
List of Figures	iv
Acknowledgement	v
Introduction	1
The Process	2
Materials Balance	8
Marketing Possibilities	9
Preliminary Investigation of Cyanide Removal from Spent Oxide	13
Conversion of Ferrocyanides with Weak and Strong Bases	17
Study of Industrial Applicability of Cyanide Extraction Process	24
Practical Application of Cyanide Extraction Process	39
Cyanide Recovery	40
Sulphur Removal	40
Sulphur Recovery	43
Summary	46
Bibliography	49
Appendix	
Table I	51
Table II	53
Table III	55

LIST OF FIGURES

Figure 1. Iron Oxide Gas Purifier	Page 4
Figure 2. Ferrocyanide Conversion vs. Lime Consumption	26
Figure 3. Ferrocyanide Conversion vs. Alkalinity	28
Figure 4. Ferrocyanide Conversion vs. Excess Lime	30
Figure 5. Ferrocyanide Conversion vs. Lime Consumption, Excess Lime and Alkalinity from Series W	32
Figure 6. Effect of Sodium Sulphate on Ferrocyanide Conversion, Excess Lime and Alkalinity, from Series X	34
Figure 7. Ferrocyanide Conversion vs. Lime Consumption, Excess Lime and Alkalinity from Series Y	36
Figure 8. Effect of Sodium Sulphate on Ferrocyanide Conversion, Excess Lime and Alkalinity, from Series Z	38
Figure 9. Sulphur from Spent Oxide, 256X	45
Figure 10. Sulphur from Spent Oxide, 1560X	45
Figure 11. Flowers of Sulphur, 256X	47
Figure 12. Ground Brimstone, 256X	47

ACKNOWLEDGEMENT

The writer wishes to acknowledge the valuable suggestions and constructive criticism offered by E. L. Hall, Operating Manager of the Portland Gas and Coke Company, and N. H. Wardale, Plant Superintendent. The assistance and generous cooperation rendered by Dr. J. F. G. Hicks, deceased, and Messrs. H. O. Ervin and A. G. Ross, laboratory coworkers, also materially aided the development of the process to its present stage.

A STUDY OF BY-PRODUCT RECOVERY FROM SPENT IRON OXIDE GAS PURIFYING MATERIAL

INTRODUCTION

Coal and oil, the materials most commonly used in the manufacture of fuel and illuminating gas, consist of complex hydrocarbons containing appreciable quantities of the elements sulphur, nitrogen, and oxygen, aside from the major constituents, carbon and hydrogen.

During the thermal decomposition of the mentioned raw materials in the production of manufactured gas, portions of said sulphur, nitrogen, and oxygen appear in combination with carbon and/or hydrogen as gaseous products, the balance entering the liquid and solid products of the reactions.

It is only the gaseous products of these elements that are of most concern to the gas manufacturer, for they constitute the major portion of what he considers undesirable constituents or impurities. The complete removal or reduction to permissible or desirable limits of these so-called impurities constitutes one of the major functions of an efficiently operated and progressive gas manufacturing plant.

The list of sulphur, nitrogen, and oxygen compounds present in raw manufactured gas is quite large. Since this investigation is concerned only with products normally re-

moved by modern so-called "purification" processes, let it suffice to simply mention the most undesirable impurities that these processes are designed to remove or reduce, namely hydrogen sulphide and hydrocyanic acid.

While the numerous other compounds of the mentioned elements may logically be considered impurities, their influence is less detrimental. Consequently, these are generally looked upon as unavoidable diluents, although some of the most modern plants do make a concerted effort to reduce carbon bisulphide, thiophene, nitric oxide, etc., to as low a limit as possible with auxiliary purification equipment.

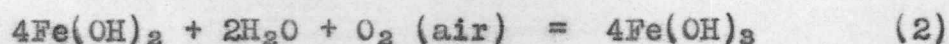
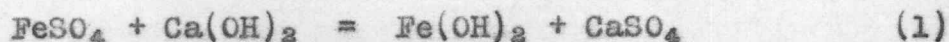
The complete removal of hydrogen sulphide and at least partial reduction of hydrocyanic acid is then the main object of practically all of the so-called purification processes applied to manufactured gas.

These processes may be applied either in the liquid or solid phase. Since the objective of this investigation was the recovery of by-products from spent solid phase purification material, only the latter method of purification need be described.

THE PROCESS

The active ingredient in the particular type of solid phase purification material under investigation is hydrated iron oxide. This is prepared by precipitation from ferrous

sulphate or copperas, and hydrated lime. The reactions involved are as follows:



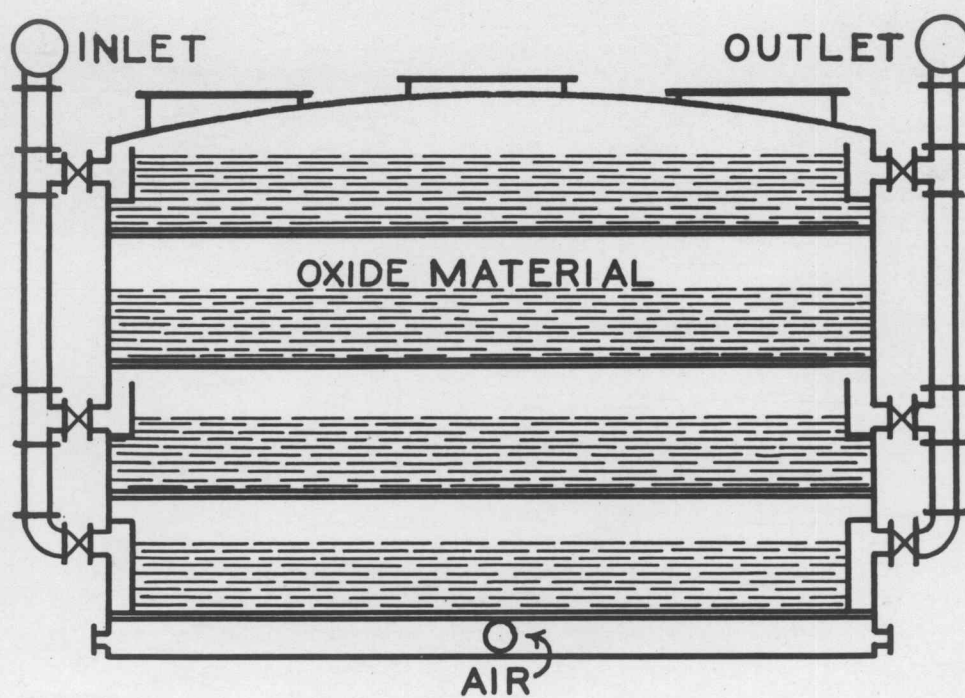
The particular material with which this investigation is concerned was prepared in batches by thoroughly mixing selected fir wood chips with slaked lime in a concrete mixer, and then adding thereto a solution containing commercial (90%) copperas dissolved in water. Thus the ferrous hydroxide was precipitated in presence of the chips, to which it adhered tenaciously in combination with the inactive calcium sulphate. Upon simple exposure to air, the ferrous hydroxide then oxidized to the ferric state, evidenced by a change in color from dark green to rust red.

The iron oxide thus spread in a thin layer over a very large surface area of loosely packed material, was then in condition for use in the aforementioned purification process. The ingredients given were used in a proportion to give material approximating 13% by weight of Fe_2O_3 on a dry basis.

The particular type of purifier used at the Portland Gas and Coke Company, Portland, Oregon, where this investigation was undertaken, is diagrammatically illustrated in Figure 1. The outer shell consists of a steel tank 32

FIGURE 1

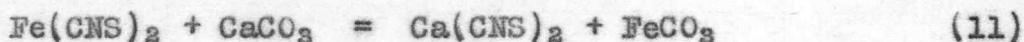
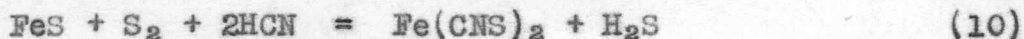
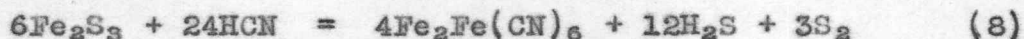
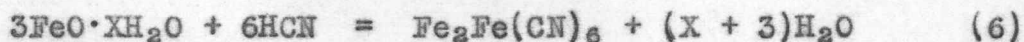
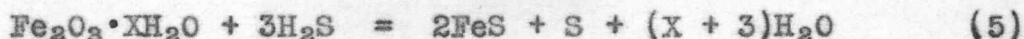
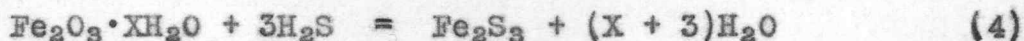
IRON OXIDE GAS PURIFIER



feet in diameter and 20 feet high. The bottoms of the four sections are made of wooden slats bolted together to form a porous support for a thin layer of excelsior. The fresh purifying material is packed into each of these sections to a depth of approximately 30 inches.

In the plant mentioned, having a maximum gas output of 30 million cubic feet per day, 16 such purifiers are installed.

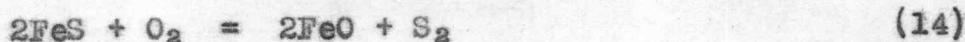
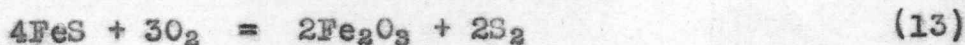
The method of applying the process consists of passing the raw gas from top to bottom of as many purifiers as required for the particular gas sendout. During this phase of the purification cycle, the primary reactions ⁽³⁾ involved concerning this investigation are as follows:



Each purifier is normally left in service for a period of 24 hours, during which time about 4 million cubic feet or less of gas are passed through. While this amount of gas is ordinarily not sufficient to completely saturate all the contained oxide material with hydrogen sulphide,

the purifiers in service are never-the-less taken from service after that period of operation for regeneration or re-vivification while another set of an equal number of regenerated purifiers are simultaneously put back into service. Thus with two sets of purifiers alternately in service and off for regeneration each 24-hour period, a continuous purification process is provided.

During the regeneration period, air is passed into the bottom of each purifier and upward through the purifying material. The oxygen of the air reacts with the sulphided iron to regenerate the oxide with liberation of free sulphur (s) in accordance with following equations:



The iron oxide combined with cyanide through reactions (6), (7), (8), (9), and (10), is not reverted to the oxide by this regenerative process. These compounds are therefore cumulative.

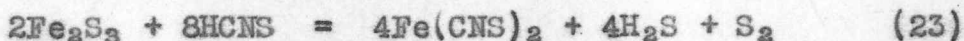
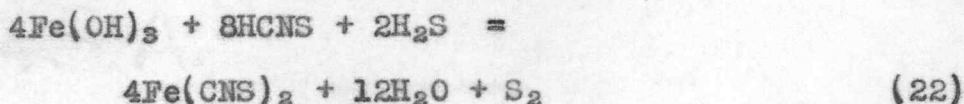
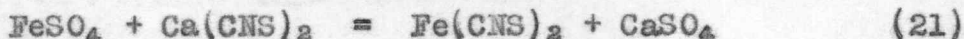
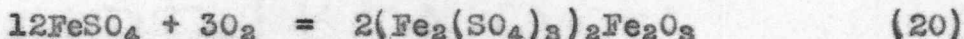
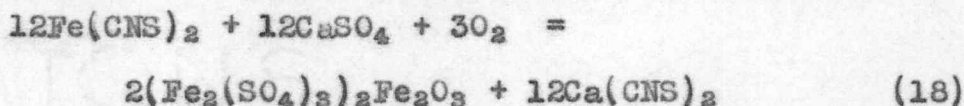
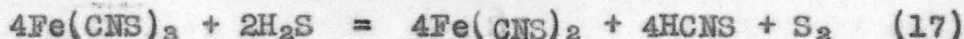
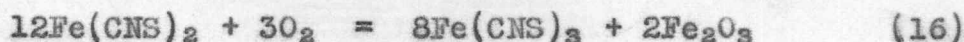
Through the medium of iron oxide, the sulphide removal process may then be simply expressed as follows:



While gas manufactured from oil contains little or no ammonia, the spent oxide recovered in purifying same is known to contain appreciable quantities of combined ammonia. This may be an accumulation of a trace formed in the crack-

ing process, or to ammonia formed by conversion of cyanides under the existing operating conditions.

Numerous other side reactions ⁽³⁾ are known to take place, among which may be mentioned the following:



These reactions are of comparatively minor importance under normal working conditions but are never-the-less significant in that they show additional methods by which iron may be inactivated and lost from useful service. The sulphocyanides being readily soluble, readily dissolve in the condensate formed in purifiers and in the water used to wet down the material during each regenerating period. They are thus capable of being washed from the system and account for a major portion of the loss of iron from purifying material during service.

During the life of the iron oxide material, the constant accumulation of free sulphur and the constant inacti-

vation or loss of a portion of the iron oxide by reaction with hydrocyanic acid, ultimately render the material so inactive that a purifier charge is no longer able to completely remove the hydrogen sulphide from a normal throughput of raw gas. When this condition arises, usually after approximately one year of normal service, the purifier is regarded as "spent" and the material removed therefrom.

Approximate analyses of fresh and spent oxide material on dry basis, are as follows:

	FRESH OXIDE MATERIAL	SPENT OXIDE MATERIAL
Iron as Oxide, Fe_2O_3	13% by wt.	5.0 % by wt.
Calcium Sulphate, CaSO_4	30	12.0
Wood Chips	57	30.0
Free Sulphur		50.0
Tar, Naphthalene, etc.		2.4
Cyanogen as Ferrocyanide		0.4
Cyanogen as Sulphocyanide		0.2
	<u>100</u>	<u>100.0</u>

MATERIALS BALANCE

The average of numerous determinations of hydrogen sulphide and hydrocyanic acid content of raw gas, and analyses of numerous batches of spent oxide material and wash liquors drained from bottom of purifiers during service, formed the basis for the approximation of the following materials balance:

INPUT	TONS, ANNUALLY	
Based on 4,300,000,000 cu. ft. of Raw Gas, Annually	Sulphur as Free Sulphur	Cyanide Materials as Cyanogen, $(\text{CN})_2$
At 310 gr. H_2S /100 cu. ft.	950	42.5
At 15.5 gr. HCN /100 cu. ft.	<u>950</u>	<u>42.5</u>

OUTPUT	TONS, ANNUALLY	
	Sulphur as Free Sulphur	Cyanide Materials as Cyanogen, (CN) ₂
1,800 Tons Spent Oxide at 50% Free Sulphur	900	
Sulphocyanides in Spent Oxide	6.1	4.9
Sulphocyanides in Wash Liquors	13.4	10.9
Cyanide as Ferrocyanides		8.8
HCN Not Recov. by Purifiers, 10%		4.3
Loss and Unaccounted For	<u>30.5</u>	<u>13.6</u>
	<u>950</u>	<u>42.5</u>

While the agreement in sulphur input and recovery is quite satisfactory, the loss and unaccounted for cyanide material appears rather large. Whether this loss is actually as large as indicated requires further confirmation.

The possible conversion of some hydrocyanic acid into other complex organic and inorganic compounds has not been fully investigated. Never-the-less, the figures presented covering only the annual output, in combination with the fact that spent oxide accumulated in a storage pile over a period of 22 years is also available for recovery, gave sufficient evidence that an adequate source of supply is available for a fair sized by-product industry.

MARKETING POSSIBILITIES

The potential annual output of over one thousand tons of sulphur material and 50 or more tons of cyanide, presented a marketing problem of no small magnitude.

An investigation of the larger markets for sulphur materials in the Pacific Northwest showed the following possible outlets:

1. As free sulphur for use in sulphite production.
2. As lime-sulphur spray material.
3. As ground agricultural sulphur.
4. As pulverized dusting sulphur.

The chief outlets for cyanides were found to be:

1. As iron blues in ink and pigment production.
2. As hydrocyanic acid for fumigation.
3. As sulphocyanide salts.

The recovery of sulphur from spent oxide material for use as a substitute for common brimstone was studied first. Preliminary tests on extraction with solvents, distillation with superheated steam and removal by simple melting were applied, but in each instance a comparatively impure and inferior product resulted. Sufficient tarry matter and resinous material from wood were present to contaminate the solvent extract. The reaction of sulphur with organic matter produced foul smelling and corrosive products during distillation. And upon melting the sulphur, only a small yield of very impure material contaminated with iron compounds, calcium sulphate and other materials, resulted. The production of a sulphur of suitable quality to be competitive with brimstone in all of its fields of application was therefore not a simple matter. Furthermore, the very low price of brimstone did not make this market particularly attractive.

The use of the spent oxide material directly for

production of sulphur dioxide for sulphite manufacture at paper mills was also considered, but even this simple method of utilizing the material did not offer much promise. Objections were excessive transportation costs and lack of sufficient storage capacity at established mills for such a bulky product comparatively low in sulphur content. The very high proportion of non-combustible matter would also create an ash nuisance, as well as a dust problem in furnace gases.

Preliminary attempts to produce a lime-sulphur solution direct from spent oxide likewise showed little promise. The recovery of a satisfactory solution from liquor containing extremely finely divided solid and colloidal matter presented some difficulties which, though not insurmountable, offered a sufficient handicap to likely render the process unprofitable in competition with lime-sulphur solutions made with the very cheap brimstone.

The use of the sulphur material for agricultural and dusting purposes gave most promise. For this purpose, a sublimed, finely ground, or pulverized sulphur is required. As a matter of fact, brimstone is not even recommended for the manufacture of the finer grades of dusting sulphur. Chemical precipitation of sulphur has become the accepted method of preparing materials fine enough to meet these exacting requirements. Since the sulphur in spent oxide material is a precipitated form, it was quite evident that

this sulphur should then be especially adapted to the production of dusting sulphur. Furthermore, the fact that these extremely fine sulphurs were bringing prices as high as a hundred dollars or more per ton, also made this outlet appear far more attractive.

Before the sulphur from spent oxide could be recommended for agricultural use, the question as to the injurious effect of the contained cyanides also needed study. References were found on the injurious effect of excessive quantities of sulphocyanide upon vegetation (2) but no information was uncovered on the effect of insoluble ferrocyanides. The effect of other cyanogen compounds (9) was also not known.

To prevent any criticism, prejudice, or injury that might result from marketing a dusting sulphur containing cyanide material, the decision was made to remove all cyanides as completely as possible.

The research program finally laid out then covered first, the complete removal of cyanide materials from spent oxide as a whole or the recovered sulphur material alone; and second, the preparation of a sulphur material of a quality suited to agricultural and dusting requirements.

While the market for dusting sulphur was rather limited, it was felt that this was largely due to the high cost of materials then available. If a material of satisfactory quality could be made from spent oxide on a small

scale at a cost not exceeding the price of competitive materials, the probability of working up a market to absorb the entire output appeared quite promising in view of the established insecticidal and fungicidal properties of these fine dusts.

With reference to the cyanides, while the materials balance showed only 32% of the available cyanogen compounds in raw gas to be present in the finally recovered spent oxide, their complete removal from same might form the nucleus for a cyanide by-product recovery process. A preliminary survey indicated the conversion of ferrocyanides to sulphocyanides and vice versa, to be commercial practices (9). However, since the outlet for cyanogen compounds as iron blues appeared most promising, the investigation was planned toward the development of this particular by-product.

PRELIMINARY INVESTIGATION OF CYANIDE

REMOVAL FROM SPENT OXIDE

As previously pointed out, the cyanides in spent oxide material exist chiefly as sulphocyanide, ferrocyanide, and carbonylferrocyanide salts. The problem of sulphur recovery was therefore concerned with the removal of these compounds from either the oxide material as a whole, or the sulphur material alone after separation from the chips.

The problem of sulphocyanide removal was a simple

matter because of the great solubility in water of the calcium and iron salts. Simple leaching of the material with water sufficed to wash it free of these compounds.

The removal of the insoluble ferrocyanide and carbonylferrocyanide salts was a more difficult matter. These could be converted to sulphocyanide and subsequently leached out by digesting the spent oxide under a steam pressure of about 30 lb. per square inch in presence of an excess of slaked lime ⁽⁹⁾. But this method was not applicable to the purpose at hand because at the temperature of the steam under 30 lb. pressure, the sulphur would fuse and lose its fine particle size.

Conversion of the ferrocyanides and carbonylferrocyanides to hydrocyanic acid by fusion with metals or by boiling in strong mineral acids ⁽⁹⁾ also presented itself, but these methods were likewise judged inapplicable or undesirable in the presence of the extremely fine sulphur material and organic matter.

Extraction of the ferrocyanides and carbonylferrocyanides after conversion by alkalis to soluble salts, then appeared to offer the most promising means for their removal. An investigation of this method of removing the insoluble cyanides in spent oxide was then undertaken.

Possible reactions of alkaline solutions on spent oxide material were studied and grouped as follows:

- (1) Conversion of insoluble ferrocyanides to soluble

salts.

(2) Precipitation of iron and part of the calcium from solution as hydroxides.

(3) Reaction with sulphur to form sulphides and polysulphides.

(4) Reaction with sulphocyanides and ammonium salts to liberate ammonia.

(5) Reaction with wood resins and other organic matter to form water-soluble or colloidal matter.

The problem was to study the conditions favoring reaction (1) in preference to all others.

As noted by Williams (⁹), other obstacles in the problem are the great cost of labor and of plant necessary to handle the very large bulk of material which contains only a few percent of ferrocyanides. The extraordinary difficulty of decomposing and recovering the ferrocyanide complexes in the spent oxide is enormously increased by the presence of free sulphur, which if not completely removed before attempting to extract the ferrocyanides with alkalis, will ordinarily pass into solution combined with the alkali as polysulphide; and not only neutralize, and therefore waste some of the alkali and greatly retard further extraction, but convert some of the ferrocyanide into sulphocyanide with consequent loss. The economical extraction of the ferrocyanides in the presence of the sulphur then presented many complications. The suggested

simplification of the problem by first extracting the sulphur with solvents was, of course, inapplicable for reasons previously mentioned, namely the destruction of the very fine particle size of the sulphur material.

Preliminary tests on liquors drained from thoroughly watered spent oxide material showed them to be very acid, generally ranging below 4.0 in pH value. Preliminary analyses indicated the liquors to consist chiefly of iron, calcium and magnesium as sulphocyanide, sulphate and thiosulphate salts. Some free acid was also indicated.

Preliminary tests on ferrocyanide conversion and extraction showed that all the iron normally present in the aqueous extract as sulphocyanide, sulphate and thiosulphate, could be precipitated from solution by adding sufficient alkali to raise the pH value of the liquor to or near the neutral point. As more alkali was added, the spent oxide was observed to gradually change in color from greenish-blue to brown, indicating the conversion of iron blues to soluble salts. As still more alkali was added, the formation of a scum on the surface, deepening in color of the solution, and positive tests for sulphide and polysulphides, indicated the beginning of the attack of alkali upon the sulphur. At this stage, a material increase in the amount of organic matter causing turbidity in the liquor also appeared.

The indication that the ferrocyanides were apparently

rendered soluble within a pH range below that forming excessive amounts of the undesirable sulphides, polysulphides and soluble organic matter, was of great significance since one objective of this investigation was to obtain a ferrocyanide liquor of sufficient purity to permit direct precipitation of iron blues, if at all possible.

The preliminary tests also indicated that the small proportion of carbonylferrocyanides would be converted to soluble salts simultaneously with the ferrocyanides. The process of removing the latter would therefore also remove the former, thus making a separate consideration of the problem of carbonylferrocyanide removal unnecessary.

The proportion of carbonylferrocyanide was found to be generally less than ten percent of the total ferrocyanide content of the spent oxide material. To simplify the tests and analyses on removal of cyanides from spent oxide, the carbonyl compound was therefore included with the other ferrocyanides.

CONVERSION OF FERROCYANIDES WITH WEAK AND STRONG BASES

The foregoing tests led to the thought that some of the weaker bases might give the proper pH value in comparatively concentrated or even saturated solution to both neutralize the liquor and extract only the ferrocyanides from the spent oxide material without forming the undesirable compounds found at the higher pH values. The sodium

carbonates, phosphates and silicates, calcium and magnesium carbonates, and magnesium oxide were considered as possibilities. But the sodium carbonates, phosphates and silicates had to be eliminated from further consideration because of their reaction with calcium salts to form less soluble compounds than calcium sulphate. Since the spent oxide material contains an appreciable quantity of the slightly soluble calcium sulphate, any alkali capable of forming a less soluble calcium salt than the sulphate would then have to be added in sufficient quantity to completely convert all of the contained calcium sulphate to the less soluble salt before the concentration of the base could build up sufficiently to give the desired pH value.

As an example, while soda ash would satisfactorily convert iron blues to soluble sodium ferrocyanide in a solution free of calcium sulphate, no such conversion was found to take place in presence of calcium sulphate until all of said sulphate, having a solubility of 0.23% by weight at atmospheric temperature, was converted to the carbonate, having a solubility of only .0065%.

In the search for the cheapest possible materials that might be used for cyanide extraction, ground Dolomite and magnesia were considered. The former, containing approximately 40% calcium carbonate and 60% magnesium carbonate, gave a solution with pH value of 8.6 when boiled in distilled water. The magnesium oxide gave a solution

with pH value of 11.4. While this value was in the range previously found conducive to the formation of sulphides and polysulphides with caustic soda, the fact that magnesium does not form a stable sulphide in aqueous solution stood in its favor.

Series of qualitative tests were then made to more thoroughly investigate the characteristics of the cyanide extracting process with both weak and strong bases. The data and results are given in Table I of the Appendix.

A study of these data and results led to the following deductions:

(1) In the presence of spent oxide in boiling water, the Dolomite is unable to provide sufficient alkalinity to convert the iron blues to soluble salts. In the presence of unleached spent oxide high in sulphocyanide, sulphate and thiosulphate content, a pH value of only 5.6 was attained (Series C) with sufficient Dolomite present to normally at least neutralize the liquor. At this low pH value, not even the iron was completely precipitated from the liquor. In the presence of partially leached spent oxide lower in salt content, a higher pH value of 6.8 was attained (Series A) with a very large excess of Dolomite. In this case, complete precipitation of iron from the acid liquor took place. The indications then were that the salts present in spent oxide liquor prevent the complete hydrolysis of the magnesium and calcium carbonates and thus

suppress the pH value. The possibility of the appreciably soluble magnesium carbonate converting the calcium sulphate present in spent oxide to the less soluble calcium carbonate, also presented itself but this was apparently not the chief cause for the condition noted because even in the presence of almost equal weights of Dolomite and spent oxide, the pH value still remained at only 6.8 (Series A).

(2) In the presence of partially leached spent oxide in boiling liquor, magnesia will serve to precipitate all the iron from the acid solution as well as cause conversion of iron blues to soluble salts. A maximum pH value of 9.0 was attained in the liquor with this alkali (Series B and D), with no indication of sulphide formation.

(3) Complete precipitation of the dissolved iron in the acid liquor from spent oxide takes place at pH values in the proximity of 6.5 (all series of tests).

(4) In the absence of a strong concentration of soluble salts from spent oxide, the conversion of iron blues begins at a pH value within the range of 7.7 to 8.2 (Series B, D, E, F, and I), but in presence of the normal concentration of these salts, conversion of ferrocyanide does not begin until pH values in the proximity of 9.2 are attained (Series G and H).

(5) Caustic soda begins to form turbid liquor at pH values in the proximity of 9.0 (Series E, F, G, H, I and J).

(6) Caustic soda begins to form an excessive amount of sulphides and polysulphides at pH values in the proximity of 9.4 and above (Series E and H), when liquor is hot, but with liquor at atmospheric temperature, this tendency is greatly reduced (Series J and K).

(7) The time element is an important factor in the cold extraction of ferrocyanides from spent oxide (Series K).

The most significant points brought out by the foregoing tests appeared to be that the soluble salts from spent oxide consume considerable alkali, that they greatly depress the pH value of the liquor, and that in the presence of the normal concentration of these salts, the extraction of ferrocyanides is greatly retarded. The results indicate further that in order to successfully and economically convert the iron blues to soluble salts within a pH range below that producing excessive sulphide formation, practically complete removal of the sulphocyanides, sulphates and thiosulphates should be effected by first thoroughly leaching the spent oxide with water before attempting ferrocyanide extraction.

Preliminary quantitative tests using caustic soda and hydrated lime for ferrocyanide extraction indicated the latter to be inferior, but upon more careful investigation, it was discovered that hydrated lime would be as satisfactory as the caustic soda if sufficient time be al-

lowed for all the lime to react. The time element then appeared to be a more important factor in lime than in caustic extraction of ferrocyanides, most likely because of the lesser solubility of the former.

A second series of quantitative tests was then made to study the effectiveness of alkalis alone and with buffer salts. The data and results are given in Table II of the Appendix.

Analysis of the various liquors was made by first separating the ferrocyanides from the sulphocyanides by precipitating the former as Prussian blue and carbonyl violet. The thoroughly washed precipitate was reconverted to the soluble potassium salts and finally electrometrically titrated with zinc sulphate ⁽⁴⁾. The filtrate was tested for sulphocyanide by the Volhard method ⁽⁸⁾.

A study of these results led to the following deductions:

(1) Thorough leaching of spent oxide before ferrocyanide extraction will cut the alkali requirement almost in half (Series L).

(2) A high recovery of ferrocyanides is not possible with caustic soda in hot solutions without forming an excessive amount of sulphides (Series L).

(3) Magnesium oxide alone or in presence of sodium sulphate will not completely extract the ferrocyanides from spent oxide (Series M, Tests 6 and 7; Series N, Test 9).

While the sodium sulphate in presence of the magnesium oxide effected an increase in pH value of the liquor, the increase in ferrocyanide recovery was only slight.

(4) A mixture of caustic soda buffered with magnesium sulphate to reduce the pH value of the solution when an excess of caustic be added, is not as effective as caustic soda alone for ferrocyanide extraction in cold solution (Series O, Tests 10 and 12), but in hot solution, the mixture appears equally effective if not somewhat superior (Series P, Tests 14 and 15). The same appeared true of the lime-magnesium sulphate mixtures (Series P, Tests 17 and 18).

(5) Excessive sulphide formation can be largely prevented by either extracting the spent oxide at atmospheric temperature, or in hot solution in presence of magnesium sulphate buffer salt (Series P).

(6) A high recovery of ferrocyanide can be attained with lime in either hot or cold solution if sufficient agitation and time be given to permit the reaction to complete itself (Series O and P).

The results of all the foregoing tests indicated quite clearly that removal of soluble salts from spent oxide before treating same for ferrocyanide removal would be highly advantageous in many ways. Such a method of treatment would consume the least amount of alkali, give a higher recovery of ferrocyanide for a given alkali consumption,

and yield purer liquors for subsequent cyanide recovery.

Since a very large proportion of the cyanide removed in purifier system escapes as sulphocyanide in purifier wash liquor, this liquor and the spent oxide wash liquor might advantageously be combined for treatment in the recovery of sulphocyanides. The ferrocyanide liquor could then be treated separately for the recovery of its cyanide content.

STUDY OF INDUSTRIAL APPLICABILITY OF CYANIDE EXTRACTION PROCESS

A final series of tests was then made to determine the efficacy of the pH method for industrial control and to further study the course of the reactions involved. Because hydrated lime had been found to be quite as satisfactory as caustic soda for ferrocyanide conversion under proper conditions, it was deemed advisable to carry on further investigations with this alkali alone, since its price is considerably below that of caustic soda.

This brought up a matter mentioned by Williams (9): that the addition of sufficient sodium sulphate to lime would reduce the unextracted portion of the ferrocyanide to a minimum. The explanation offered for this phenomenon is that the sodium sulphate probably salts out calcium from solution and thus prevents the formation of insoluble basic calcium ferrocyanide.

Table III gives the data and results on this last series of tests, using lime with and without sodium sulphate. In order to be able to more clearly visualize the effect of the different variables, Figures 2 to 8 were prepared.

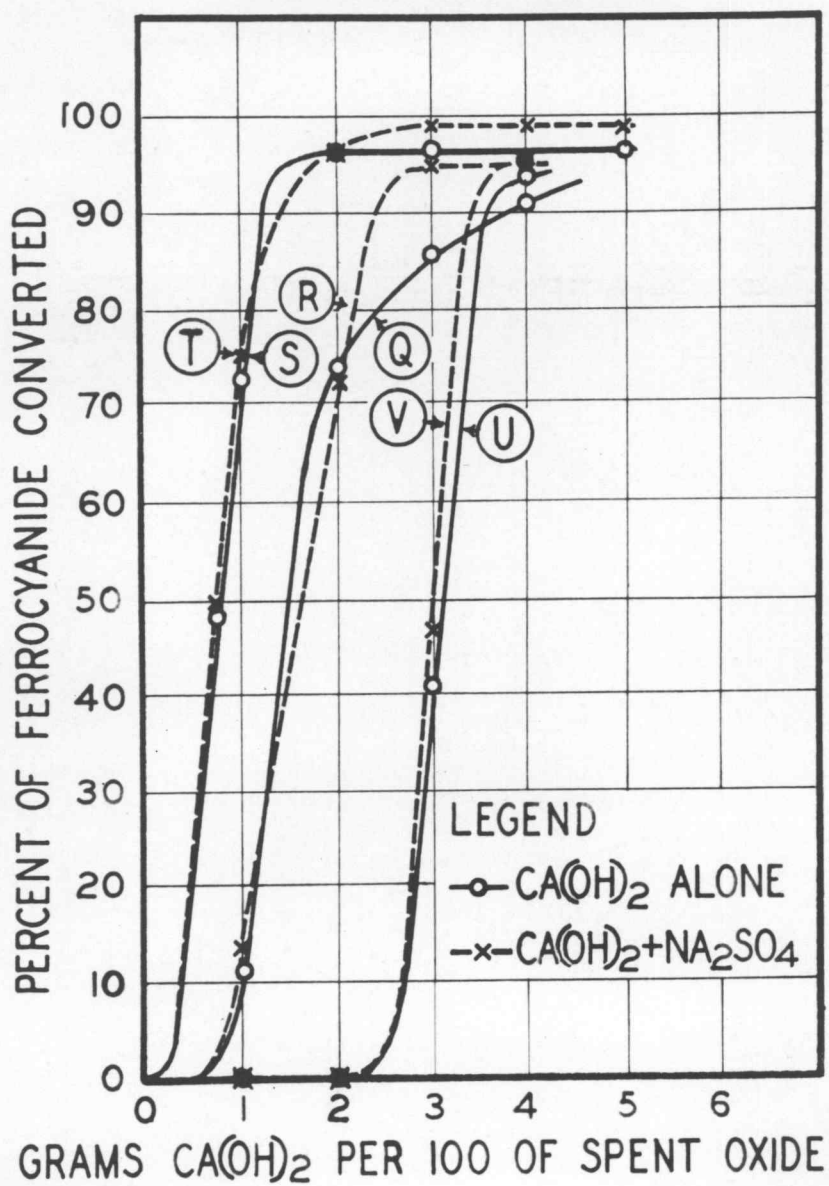
Referring to Fig. 2 and the test data pertaining thereto, the following deductions were made:

(1) The extraction of the ferrocyanides takes place most quickly and readily from spent oxide lowest in sulphocyanide content. Even though the spent oxide material used in Series S and T contained 1.42 times more ferrocyanide than that used in Series Q and R, the extraction was quicker and more complete at low concentrations of lime, apparently due to the lower sulphocyanide and associated salt content of former. Series U and V made on unleached spent oxide containing a high proportion of sulphocyanide and associated salts, required considerably more lime even though the ferrocyanide content was less than that of oxide used in Series S and T. The sulphocyanide and ferrocyanide contents of the spent oxides used in these tests are tabulated herewith to facilitate this comparison.

Series No.	% by Wt. of $(CN)_2$ as CNS	% by Wt. of $(CN)_2$ as $Fe(CN)_6$
Q and R	0.094	.328
S and T	0.035	.467
U and V	0.690	.396

Comparisons of these data and the curves in Figure 2 show quite plainly that the lime consumption is greatly dependent upon the sulphocyanide and associated salt content of

FIGURE 2
FERROCYANIDE CONVERSION
VS
LIME CONSUMPTION



these oxides, as well as on the ferrocyanide content.

(2) A starting sulphocyanide content in spent oxide of less than approximately 0.2% by weight is desirable in order to reduce the alkali consumption for ferrocyanide extraction to a minimum.

(3) Approximately 0.14 to 0.30% by weight of sulphocyanide is formed during the extraction process.

(4) In every series in which sodium sulphate was used, the percentage of ferrocyanide extracted for a given amount of lime added, was higher.

A study of Figure 3 showing the relation between percentage of ferrocyanide extracted and the pH value of liquor after sufficient time of contact had been allowed to permit the alkali to practically complete its work, led to the following deductions:

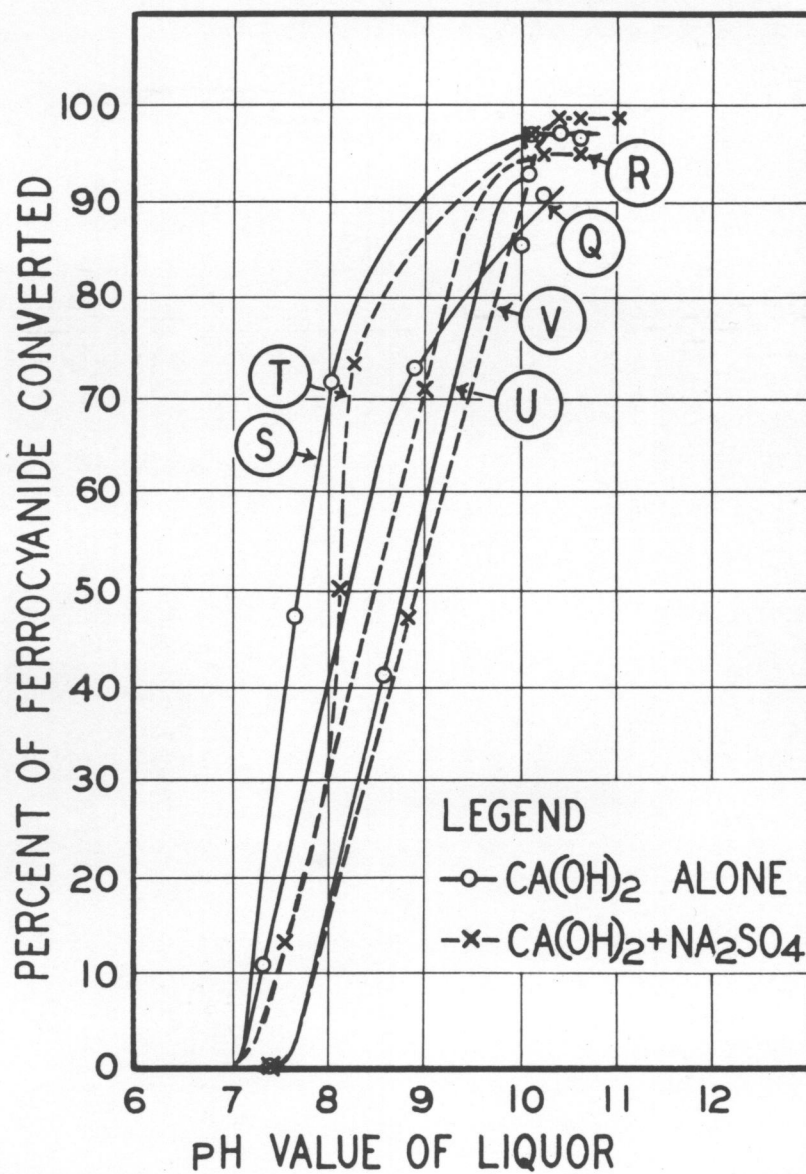
(1) In each series, the ferrocyanide extraction was practically complete when a pH value of approximately 10.2 was attained.

(2) The presence of the sulphocyanide and associated salts greatly suppresses the ferrocyanide recovery for pH values below 10.0.

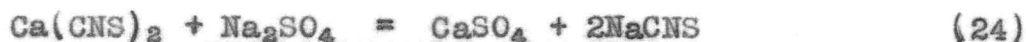
(3) The addition of sodium sulphate tends to give higher ultimate recoveries.

A study of the possible reactions that sodium sulphate might undergo in spent oxide liquor, led to the deduction that aside from the reaction mentioned by Williams

FIGURE 3
FERROCYANIDE CONVERSION
VS
ALKALINITY



(9), other reactions likely to produce the effects noted are as follows:



The first reaction would tend to convert the strongly acid calcium sulphocyanide to the more neutral sodium salt, thus tending to give the higher pH values observed. The second reaction would tend to form caustic soda, which probably more actively attacks the insoluble ferrocyanides to form soluble salts. The cycle of the reaction appears to be somewhat as follows, starting with the caustic soda and ending with the calcium sulphate from reaction (25):

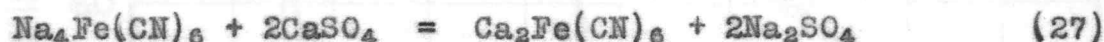


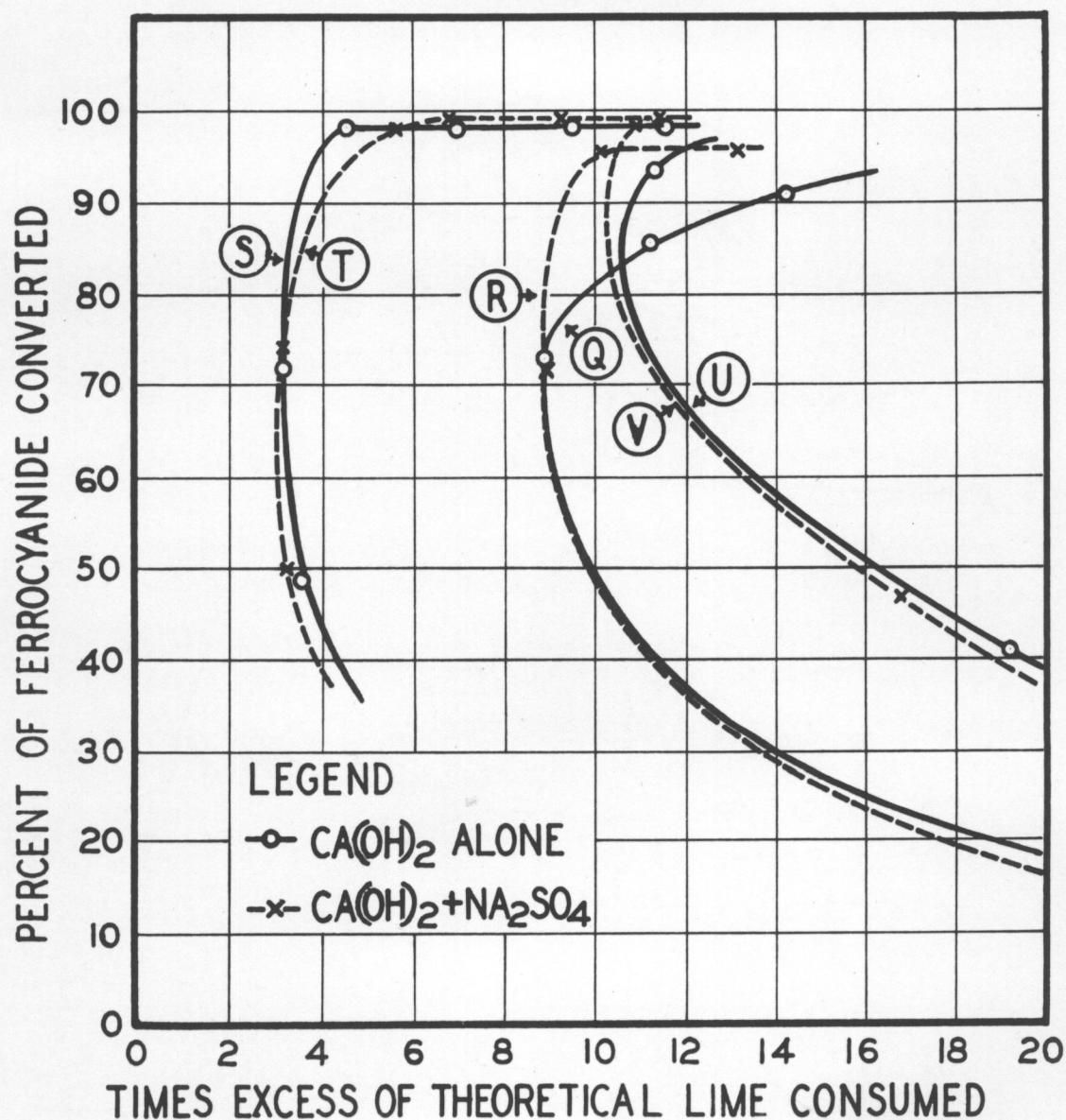
Figure 4, and data associated therewith, led to the following deductions:

(1) The spent oxide lowest in sulphocyanide content requires the least excess of alkali.

(2) The addition of sodium sulphate tends to cause a saving in alkali consumption as well as cause a higher ultimate ferrocyanide recovery.

(3) A minimum of approximately 3 to 4 times the theoretical amount of alkali seems to be the lowest consumption attainable and then only with spent oxide from which the sulphocyanide and associated salts have been thoroughly leached.

FIGURE 4
FERROCYANIDE CONVERSION
VS
EXCESS LIME



(4) From the standpoint of alkali consumption alone, a ferrocyanide recovery of 80 to 90% appears the most economical since higher recoveries require considerably greater excess of lime.

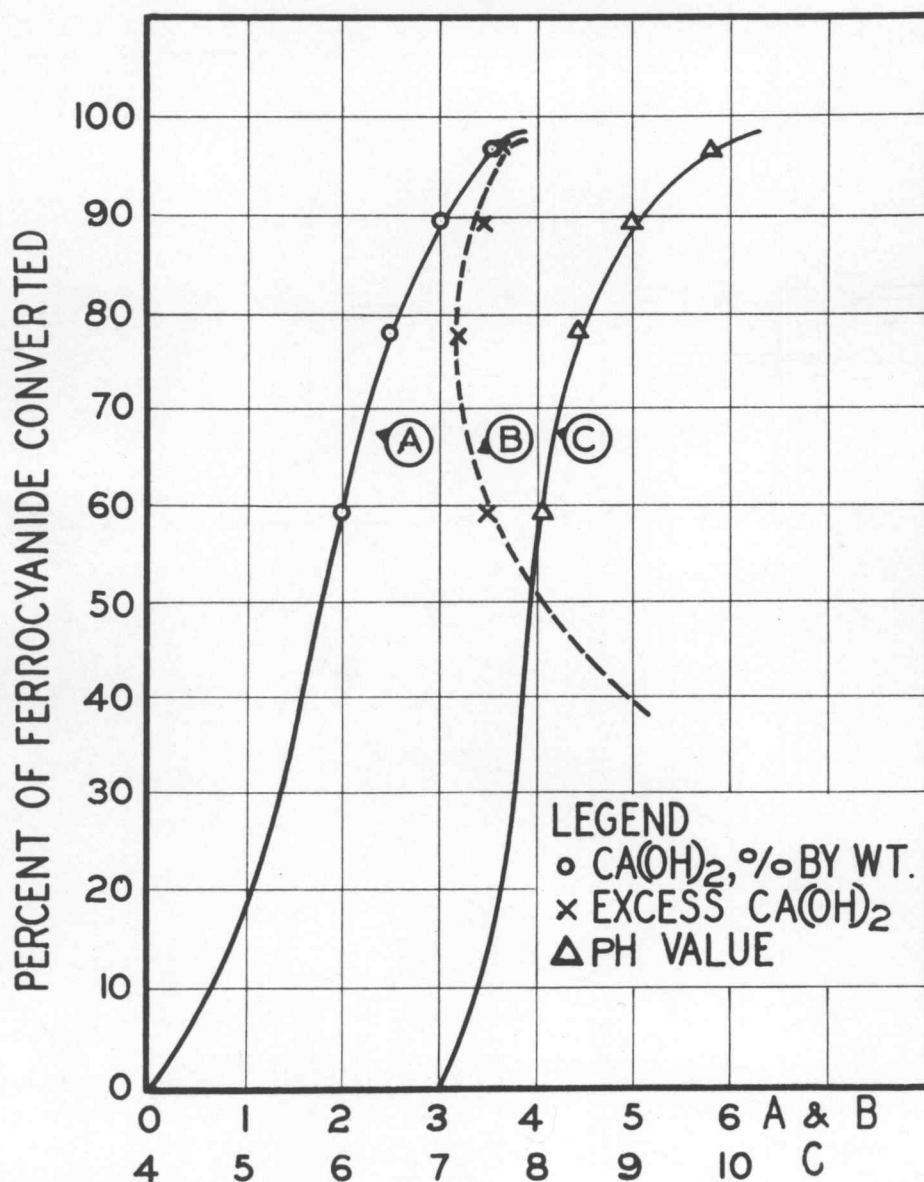
Figure 5 and its associated data from Series W based on treatment of spent oxide abnormally high in ferrocyanide content led to the following deductions:

(1) Even though the spent oxide treated in this series contained 2 to 3 times more ferrocyanide than the oxide used in previous tests, the general characteristics of the curves for pH value and excess alkali remained the same. Practically complete extraction of ferrocyanide at a pH value of 10.0 or slightly above, and an alkali consumption somewhere between 3 and 4 times theoretical, is again indicated.

(2) pH measurements afford a very simple and practical means for controlling the process irrespective of the ferrocyanide content of the spent oxide, without necessitating a resort to tedious and time-consuming analytical methods to predetermine the ferrocyanide content of each batch of spent oxide before extraction, if and only when the sulphocyanide and associated salt content of the liquor be reduced to a minimum.

Figure 6 and its associated data from tests in Series X made to determine the economy of using sodium sulphate in ferrocyanide extraction with lime from same type

FIGURE 5
FERROCYANIDE CONVERSION
VS
LIME CONSUMPTION, EXCESS LIME AND ALKALINITY
FROM SERIES W



of spent oxide material as used in Series W above, led to the following deductions:

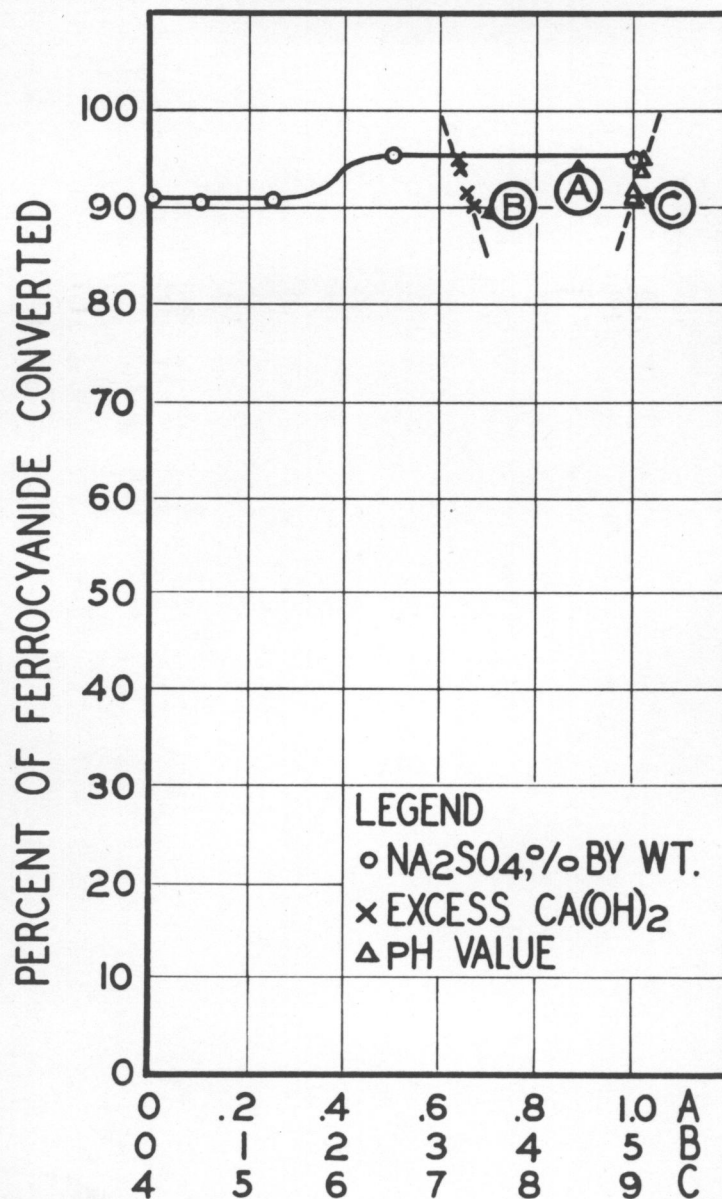
(1) There appears to be a definite increase in percentage of ferrocyanide recovery at a concentration of 0.5% by weight of Na_2SO_4 in thoroughly leached spent oxide of abnormally high ferrocyanide content. An increase of approximately 5% in the ferrocyanide recovery is indicated.

(2) The above mentioned concentration of sodium sulphate caused a slight but noticeable increase in the pH value of the liquor.

(3) With the aforementioned concentration of sodium sulphate or in excess thereof, a noticeable decrease in the excess lime required for conversion of ferrocyanides took place. A drop from 3.33 to 3.16 times excess alkali is indicated in this particular test. 0.5 gm. of sodium sulphate was effective in saving about 0.2 gm. of hydrated lime. At a price of one cent per pound for both lime and sodium sulphate, there would be no saving in using the latter to reduce alkali consumption alone. But if the apparent 5% increase in yield of ferrocyanide be taken into account, the cost of sodium sulphate would be justified if the credit of the recovered ferrocyanide would equal or exceed 5.5 cents per pound as Prussian blue. Since the price of ferrocyanide salts exceeds this figure, it appears that the use of sodium sulphate would be economically justified if the liquor be treated for cyanide recovery, but not oth-

FIGURE 6

EFFECT OF SODIUM SULPHATE ON
FERROCYANIDE CONVERSION, EXCESS LIME
AND ALKALINITY, FROM SERIES X



erwise, unless the more complete removal of ferrocyanide be essential for other reasons.

A similar series of tests was finally made on spent oxide more nearly normal in ferrocyanide content. This material was of fresher quality than that used in Series W and X, and therefore probably higher in tar and gum content. The data and results are given under Series Y and Z.

Figure 7 based on the results of Series Y, led to the following deductions:

(1) The general trend of the curves is similar to trend shown in Fig. 5 for spent oxide high in ferrocyanide content.

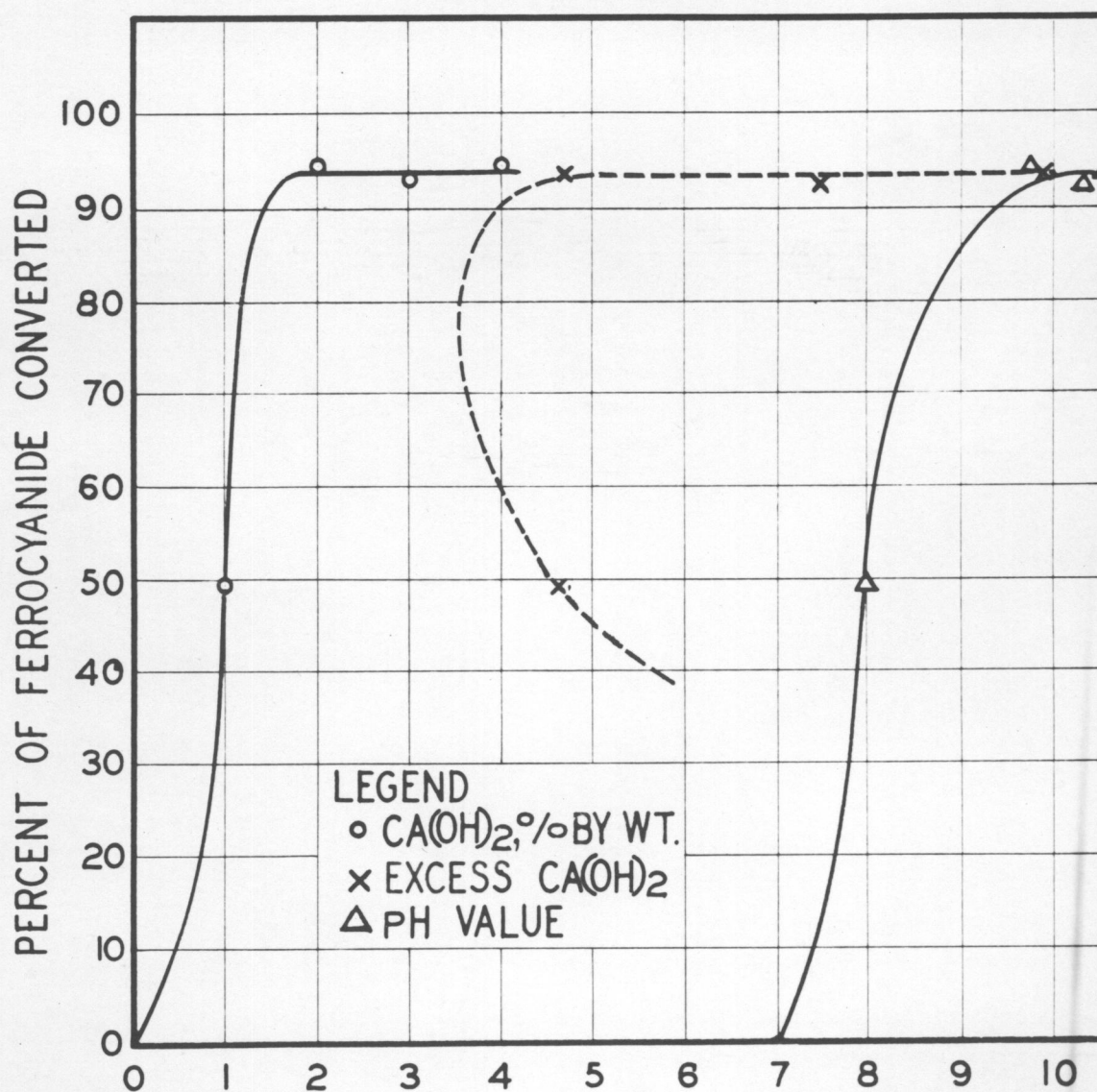
(2) Series Y gave a slightly lower final recovery of ferrocyanide and a slightly higher minimum lime consumption, which may be attributed to a higher tar and gum content of the fresher material.

(3) The pH value of the liquor was again very closely related to percentage of ferrocyanide extracted.

The deductions drawn from Figure 8 and data from Series Z, are as follows:

(1) Sodium sulphate again caused a noticeable increase in ferrocyanide recovery with lime. But in this series, the rise in recovery attained a maximum at a concentration of only approximately 0.25% by weight of sodium sulphate, or half the optimum concentration found in Series W. This suggests that the amount of sodium sulphate

FIGURE 7
FERROCYANIDE CONVERSION
VS
LIME CONSUMPTION, EXCESS LIME AND ALKALINITY
FROM SERIES Y



should probably be varied with the ferrocyanide content of the spent oxide rather than kept constant at a given percentage by weight of material treated. Since the optimum concentration in both series was attained when the ratio of hydrated lime to sodium sulphate was approximately 10 to 1, it seems that such a mixture might advantageously be used to give a maximum recovery of ferrocyanide from all grades of spent oxide where the use of sodium sulphate is at all justified for economic or other reasons. However, this deduction should be checked by further tests before final acceptance.

(2) A very large excess of sodium sulphate does not appear to be detrimental to the extraction process.

(3) The sodium sulphate again caused a slight but noticeable increase in the pH value of the liquor and a reduction in the excess lime required for the extraction.

The general conclusions drawn from all the series of tests were as follows:

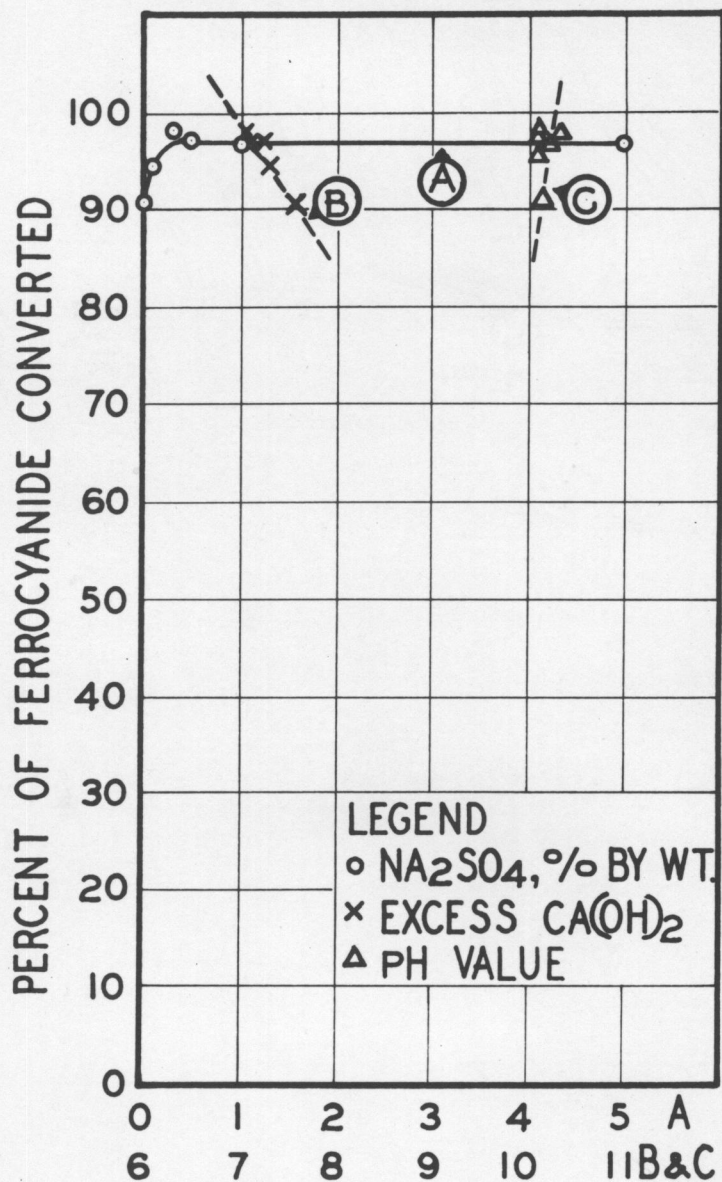
(1) Practically complete ferrocyanide extraction from all grades of spent oxide can be effected in presence of the sulphur material without undue contamination of liquors with sulphides and polysulphides.

(2) Said extraction should preferably be made after the sulphocyanides and their associated salts have been thoroughly leached from the oxide material.

(3) To attain practically complete ferrocyanide con-

FIGURE 8

EFFECT OF SODIUM SULPHATE ON
FERROCYANIDE CONVERSION, EXCESS LIME
AND ALKALINITY, FROM SERIES Z



version, addition of hydrated lime until the pH value of the slurry reaches a constant value between 10.0 and 10.5 is required.

(4) The use of sodium sulphate with lime is a definite advantage resulting in approximately 5% greater ultimate recovery of ferrocyanide. A mixture of 10 parts hydrated lime and 1 part sodium sulphate appears to give a simple formula for attaining best results.

(5) Under the above system of ferrocyanide extraction, the minimum attainable lime consumption is in the proximity of 3 to 4 times that theoretically required to combine with the extracted ferrocyanides.

PRACTICAL APPLICATION OF CYANIDE EXTRACTION PROCESS

The procedure finally adopted for removing the cyanides from spent oxide material in commercial practice, consisted of thoroughly leaching the material of soluble salts and then adding hydrated lime or a mixture of same with sodium sulphate in the proportion of 10 to 1, in small doses until a pH value of 10.0 to 10.5 persisted after prolonged agitation.

Instead of applying the more or less complicated laboratory methods for controlling the pH value of the cyanide extraction liquors, test papers were prepared by dipping blotter paper in solutions of phenol red, thymol blue, and La Motte purple and then drying same. By simply

dipping strips of these papers in the liquor while a charge of spent oxide or sulphur material was being treated with lime, the alkalinity could be followed with all the precision necessary for practical purposes. When lime was added until the thymol blue remained permanently blue and the La Motte purple showed not more than a faint tinge of pink, the extraction was judged complete. Laboratory checks showed the method to be entirely satisfactory for control purposes.

CYANIDE RECOVERY

The discussion thus far concerns only the removal of cyanides from gas purifying material during and after service. As previously mentioned, these cyanides are extracted chiefly as sulphocyanide and ferrocyanide salts. While considerable work has been done on the recovery of these cyanides from the weak liquors, the work is yet incomplete and not sufficiently conclusive to be reported at this time.

SULPHUR REMOVAL

To facilitate rapid and complete conversion of ferrocyanides in presence of tarry matter as well as assist with the more complete removal of the sulphur material from the wood chips, it was deemed advisable in practice to mechanically macerate the spent oxide material. Such a treatment was deemed essential to a high recovery because much of the

sulphur and its associated material was more or less firmly bound to the chips by the tarry or resinous matter. The problem was to remove this bound material with minimum disintegration of chips.

Numerous methods were considered ranging from simple stirring or agitation to drastic maceration. Without going into detail, these preliminary tests indicated that sufficient mechanical force would have to be applied to partially disintegrate the chips if a consistent sulphur recovery of 90% or more was to be attained.

The mechanisms tried for the purpose at hand consisted of various types of grinders, choppers, mixers, and mills. While some of the grinders and choppers gave quite satisfactory results, the fact that the spent oxide material held in storage for a good many years had become more or less contaminated with foreign matter in the form of scrap iron, concrete, rocks, etc., made their application inadvisable. Some types of mixers also would not successfully handle foreign matter of the type mentioned.

The apparatus finally selected as most suitable for the service was a ball mill. With this apparatus not only all the aforementioned foreign matter could be successfully handled, but the size, number, and weight of the balls could be varied to give the amount of maceration desired for spent oxides in various stages of decomposition. The latter was an important factor in that the strength of the

wood chips in spent oxide material held in storage many years varied over wide limits, which in turn would necessitate various degrees of maceration to insure minimum wood content of fines consistent with high sulphur recovery.

The process finally adopted consisted of first running the spent oxide material through a spring loaded lump crusher to disintegrate the larger lumps to a fine aggregate, and then feeding this crushed material into the ball mill with a stream of water.

Because cyanide recovery from the weak extraction liquors had not yet been completed when the sulphur recovery plant first went into operation, the crude slurry from the mill was simply put through a washing screen and the chips run to waste for ultimate consumption as fuel, thus to save the lime that would otherwise be consumed in treating the chips. The fine slurry containing the sulphur, iron oxide, calcium sulphate, and both soluble and insoluble cyanides, was run to leaching tanks where the aforementioned treatment for sulphocyanide and ferrocyanide removal was subsequently undertaken. The relatively small volume of cyanide liquor produced during this initial sulphur recovery operation was pumped to the top of spent oxide storage pile, thus to reprecipitate and reabsorb the cyanides in this material for future recovery.

SULPHUR RECOVERY

After the fine sulphur slurry had been treated for removal of cyanides by methods previously discussed, the problem remained to get this material into a dry form in as fine a state of division as possible.

Considerable work had been done on this problem in the production of dusting material from sulphur recovered in the liquid purification of manufactured gas (5)(6). The results of this work indicated that if said sulphur be heated in excess of approximately 170° F., its insecticidal and fungicidal properties would be materially impaired. Methods of filtering the sulphur from the liquor and subsequently drying the cake in tunnels receiving large volumes of heated air, were used.

The remarkable progress made in more recent years in the development of spray dryers for drying insecticides and allied chemicals (1) suggested this new method of treatment might advantageously be applied. By this method, materials normally destroyed at or near the temperature of boiling water have been successfully dried because of the cooling effect of the instantaneous evaporation and the extremely short time of contact of the materials to these temperatures.

Trial tests showed this type of dryer to be well suited to the purpose at hand, and led to the installation

of a commercial unit of the Peebles type spray dryer. This then solved the problem of dry sulphur recovery from sulphur slurry.

However, the sulphur material from the Peebles dryer still contained a sufficient amount of coarse material in the form of agglomerated sulphur masses to necessitate some means of further disintegrating these particles. The dried material was consequently given a final treatment in a Raymond pulverizer and air floated before final sacking.

The extremely small particle size of this final product is shown in photomicrographs, Figures 9 and 10.

The magnification in Figure 9 is 256 times and the grid spacing, 50 microns per division, approximately equivalent to the spacing of a 300 mesh sieve. As shown, practically all of the sulphur has a particle size of less than 50 microns.

Sieve analyses on tons of the material prepared for marketing, gave the following average:

On 100 mesh, Dry	0.02%
Through 100 on 200, Dry	0.11%
Total through 325 mesh, Wet	97.2 % (7)

The magnification in Figure 10 is 1560 times and the grid spacing, 8.3 microns per division. That many of the sulphur particles are one micron or less in size, is readily apparent.

For comparison, photomicrographs of flowers of sulphur and ground brimstone are shown in Figures 11 and 12,

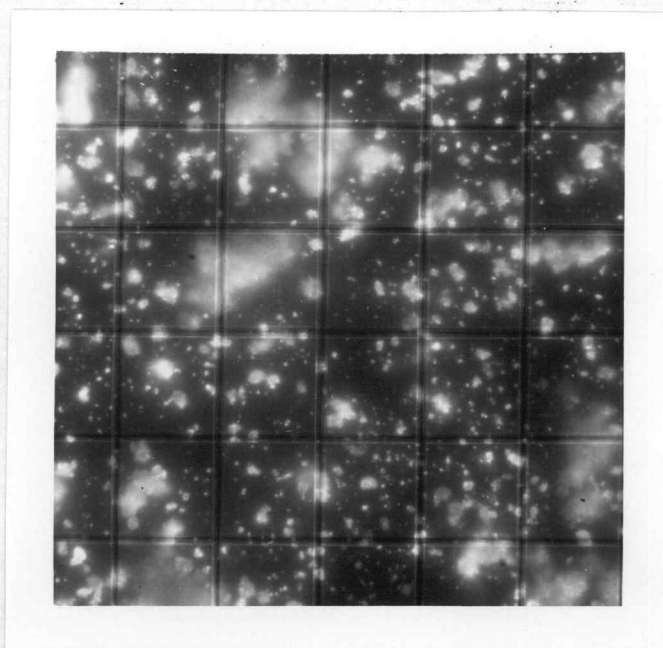


Figure 9. Sulphur from Spent Oxide.
256X
50 microns per division.

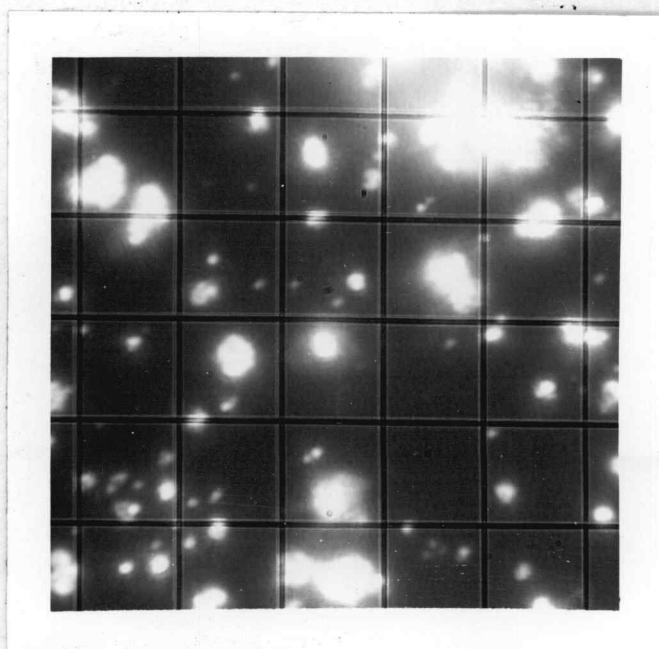


Figure 10. Sulphur from Spent Oxide.
1560X
8.3 microns per division.

respectively. Both are at 256 magnification with grid spacing of 50 microns. Comparing these with Figure 9, it can be readily seen that the material prepared from the precipitated sulphur in spent oxide material, is of much finer quality.

It is quite generally agreed that extremely finely divided sulphur is more active, aside from having enhanced dusting value, and greater adhesion. As a matter of fact, sulphur material as fine as that prepared commercially from the spent oxide material has been proven so active that the general practice has become to blend it with the coarser ground and flowers of sulphur rather than use it straight, thus to safeguard against "burning" of vegetation therewith.

Field tests on the control of Pacific mite, powdery mildew, red spider, citrus thrips, fruit scab and similar insect pests and fungous diseases, have shown very encouraging results, indicating that the sulphur material prepared as a result of this investigation and marketed under the trade name "Microsulfur", is well suited for the purpose intended.

SUMMARY

The conversion of the insoluble iron ferrocyanides present in spent oxide purification materials to soluble salts with the aid of alkalis in presence of the associ-

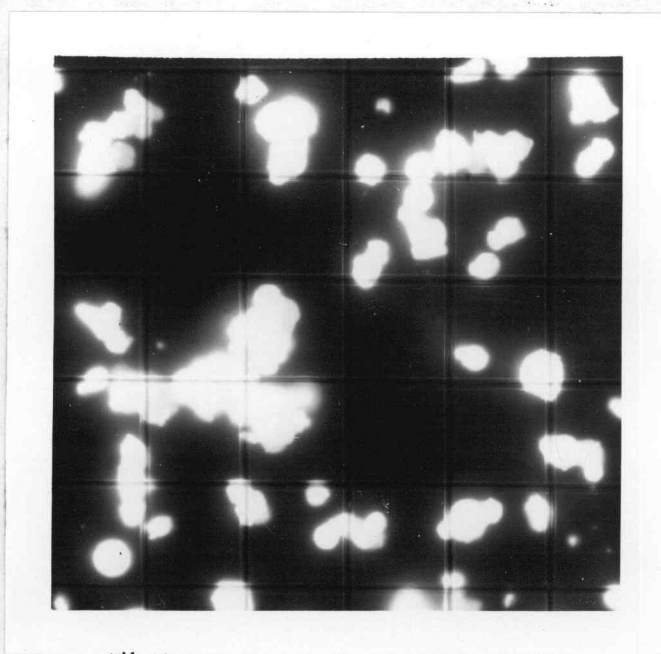


Figure 11. Flowers of Sulphur.
256X
50 microns per division.

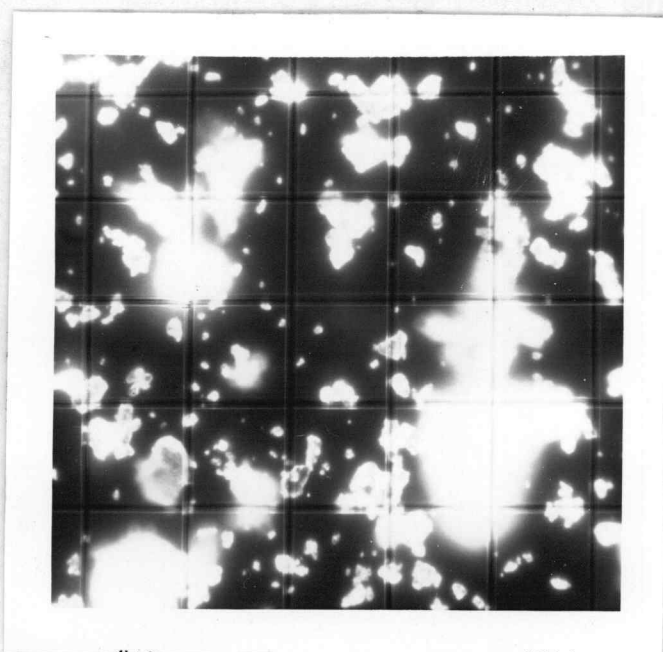


Figure 12. Ground Brimstone.
256X
50 microns per division.

ated free sulphur without the formation of undesirable sulphides and polysulphides was found commercially feasible by maintaining the pH value of the extracting liquors near but not exceeding 10.5. The method gave a minimum alkali consumption consistent with practically complete ferrocyanide conversion, without the necessity of further laboratory control, and yielded a cleaner and purer liquor for subsequent treatment in ferrocyanide recovery.

It was found that the insecticidal and fungicidal value of the sulphur present in spent oxide material was not destroyed by the process of reducing the material to a slurry and subsequently drying in a Peebles flash evaporator. A final treatment of the dried product in a pulverizer yielded a sulphur of extremely fine particle size containing a large number of particles one micron or less in size and leaving only 5% or less of residue on a 325 mesh sieve.

BIBLIOGRAPHY

1. Alford, Edwin C. Chemical and Metallurgical Engineering, 41:634-636, 1934.
2. Bourcart, E. Insecticides, Fungicides, and Weed Killers.
3. Clayton, R. H., Williams, H. E., and Avery, H. B. Gas Journal, 196:311, Nov. 4, 1931.
4. Kolthoff, I. M. and Furman, N. H. Potentiometric Titrations, John Wiley and Sons, Inc., London, 1926.
5. Proceedings of the Pacific Coast Gas Association, 1926, pp. 409-439, San Francisco.
6. Proceedings of the Pacific Coast Gas Association, 1927, pp. 250-269, San Francisco.
7. State of California, Method of the Division of Chemistry, Sacramento.
8. Sutton, F. Volumetric Analysis, p. 150, P. Blackiston's Son and Co., Philadelphia.
9. Williams, H. E. The Chemistry of Cyanogen Compounds, J. and A. Churchill, London, 1915.

APPENDIX

TABLE I

TABLE I

	Spent Oxide gm.	Materials		Water ml	Temp. °F.	Readings					H ₂ S and Sulphides	Remarks
		Alkali Type	Used Wt. gm.			pH Value	Fe ⁺⁺	CNS ⁻⁻⁻	Fe(CN) ₆ ⁻⁻⁻⁻			
Series A												
Reading No.	1	450	Dolomite	0	1500	212	4.0-	+	+	-	-	Spent oxide leached with water for CNS reduction.
	2			8			6.2	+	+	-	-	
	3			13			6.4	-	+	-	-	
	4			18			6.4	-	+	-	-	Spent oxide turning from greenish to brown color.
	5			23			6.6	-	+	-	-	
	6			48			6.7	-	+	-	-	
	7			100			6.8	-	+	-	-	
	8			200			6.8	-	+	-	-	
	9			400			6.8	-	+	-	-	Dolomite not able to put Fe(CN) ₆ into solution.
Series B												
Reading No.	1	450	MgO	0	1500	212	4.0-	+	+	-	-	Spent oxide leached with water to remove soluble salts.
	2			4			6.2	+	+	-	-	
	3			7			8.2	-	+	+	-	MgO able to put Fe(CN) ₆ into solution.
	4			10			8.8	-	+	+	-	
	5			--			9.0	-	+	+	-	After filtering off above liquor and adding fresh water.
Series C												
Reading No.	1	450	Dolomite	0	1500	212	4.0-	+	+	-	-	Soluble salts <u>not</u> leached from spent oxide.
	2			1			4.0-	+	+	-	-	
	3			2			5.0	+	+	-	-	
	4			4			5.4	+	+	-	-	
	5			11			5.6	+	+	-	-	Soluble salts suppress pH value below Series A values.
Series D												
Reading No.	1	450	MgO	1	1500	212	4.0-	+	+	-	-	Spent oxide leached with water to remove soluble salts.
	2			2			4.5	+	+	-	-	
	3			3			5.2	+	+	-	-	
	4			5			6.2	+	+	-	-	
	5			6			6.5	-	+	-	-	Dissolved iron completely precipitated.
	6			7			8.0	-	+	+	-	Trace ferrocyanide appears in liquor.
	7			8			8.4	-	+	+	-	Strong test for Fe(CN) ₆ .
	8			10			8.8	-	+	+	-	
	9			15			9.0	-	+	+	-	Some blue still visible on chips.
Series E												
Reading No.	1	450	NaOH	2	1500	150-180	4.7	+	+	-	-	Spent oxide leached for soluble salt reduction.
	2			4			6.7	-	+	-	-	
	3			5			7.8	-	+	+	-	Trace Fe(CN) ₆ .
	4			6			8.4	-	+	+	-	Strong test for Fe(CN) ₆ .
	5			8			8.9	-	+	+	-	Still some blue visible on chips.
	6			10			9.3	-	+	+	+	NH ₃ strong. Liquor turbid. Trace blue on chips.
	7			15			?	-	+	+	+	Scum on liquor. Very turbid. pH questionable.
Series F												
Reading No.	1	450	NaOH	1	1500	150-180	4.0-	+	+	-	-	Spent oxide leached for soluble salt reduction.
	2			2			4.8	+	+	-	-	
	3			3			6.0	+	+	-	-	Only trace Fe.
	4			4			6.8	-	+	-	-	Filtered off liquor and added fresh water.
	5			4			5.4	+	+	-	-	
	6			5			7.7	-	+	+	-	Fe(CN) ₆ present.
	7			6			8.9	-	+	+	-	
	8			7			8.9	-	+	+	-	Liquor still clear, no H ₂ S.
	9			8			9.3	-	+	+	+	NH ₃ , liquor turbid, trace H ₂ S.
Series G												
Reading No.	1	450	NaOH	1	1500	150-180	4.0-	+	+	-	-	Spent oxide <u>high</u> in soluble salt content.
	2			2			4.0-	+	+	-	-	
	3			3			4.0-	+	+	-	-	
	4			4			4.6	+	+	-	-	
	5			5			6.1	-	+	-	-	No Fe in solution.
	6			6			6.7	-	+	-	-	
	7			7			7.2	-	+	-	-	
	8			8			8.5	-	+	-	-	Chips brownish-green color.
	9			9			8.5	-	+	-	-	Trace NH ₃ , still no Fe(CN) ₆ in liquor.
	10			10			9.2	-	+	+	-	Still no Fe(CN) ₆ in liquor.
	11			11			9.4	-	+	+	+	Trace Fe(CN) ₆ , NH ₃ strong.
Series H												
Reading No.	1	450	NaOH	2	1500	150-180	4.0-	+	+	-	-	Spent oxide <u>high</u> in soluble salt content.
	2			3			4.0-	+	+	-	-	
	3			4			4.2	+	+	-	-	
	4			6			5.9	+	+	-	-	
	5			7			7.5	-	+	-	-	
	6			7			6.2	-	+	-	-	Filtered off liquor and added fresh water.
	7			8			7.9	-	+	-	-	
	8			9			6.8	-	+	-	-	
	9			10			8.6	-	+	-	+	2 hour interval.
	10			11			9.2	-	+	+	+	H ₂ S present. Liquor turbid.
	11			12			9.5	-	+	+	+	Fe(CN) ₆ present.
Series I												
Reading No.	1	450	NaOH	0	1500	150-180	4.0-	+	+	-	-	Spent oxide thoroughly leached for salt reduction.
	2			1			5.2	+	+	-	-	
	3			2			6.0	+	+	-	-	
	4			2.5			6.4	+	+	-	-	Trace Fe in liquor.
	5			3			6.8	-	+	-	-	No Fe in liquor.
	6			4			8.0	-	+	+	-	Fe(CN) ₆ present.
	7			5			8.7	-	+	+	+	Liquor turbid.
	8			6			9.2	-	+	+	+	No visible blue on chips.
Series J												
Reading No.	1	450	NaOH	2	1500	Atmos.	7.1	-	+	-	-	Thoroughly leached spent oxide.
	2			4			8.8	-	+	+	-	Slurry stirred 1/2 to 1 hour between pH readings.
	3			5			8.8	-	+	+	+	H ₂ S and NH ₃ present.
	4			6			8.9	-	+	+	+	Considerable blue on chips.
	5			8			9.2	-	+	+	+	Chips still contain some blue.
	6			9			9.4	-	+	+	+	Same.
	7			9			8.8	-	+	+	+	Stood overnight.
	8			10			9.4	-	+	+	+	Some blue still visible on chips.
	9			11			9.6	-	+	+	+	Same.
Series K												
Reading No.	1	450	NaOH	5	1500	Atmos.	9.6	-	+	+	-	Same as Series J, to study effect of <u>time</u> element.
	2			Same, after 1/2 hour.			7.2	-	+	-	-	Fe(CN) ₆ precipitated out.
	3			Same, after 1 1/2 hours.			5.2	+	+	-	-	Fe appears in solution again.
	4			6 after 1/4 hour.			6.5	-	+	-	-	No Fe in solution.
	5			Same, after 1 1/2 hrs.			6.0	+	+	-	-	Trace Fe in solution.
	6			6.5 after 1 hour.			7.2	-	+	-	-	Filtered off liquor and added fresh water.
	7			8.5 after 1/2 hour.			9.0	-	+	+	-	Fe(CN) ₆ again appears.
	8			9.5 after 3/4 hour.			9.0	-	+	+	-	Liquor clear, no H ₂ S.
	9			10.5 after 1 hour.			9.2	-	+	+	+	Trace H ₂ S and NH ₃ . Chips blue in spots.
	10			11.5 after 1 hour.			9.3	-	+	+	+	Same.
	11			12.5 after 1 hour.			9.6	-	+	+	+	Same.
	12			Same, after 2 hours.			9.4	-	+	+	+	Liquor clear but becomes turbid on acidifying.
	13			Same, overnight.			9.0	-	+	+	+	Same.
	14			13.0 after 2 1/2 hrs.			9.2	-	+	+	+	Same. Still some blue on chips.
	15			14.0 after 5 hours.			9.6	-	+	+	+	Same. Trace of sulphide and polysulphide.

TABLE II

TABLE II

Series No.	L					M		N		O			P					
Test No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Spent Oxide, gm., dry	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200
Water Used for Leaching, ml	1250	1250	none	none	none	none	none	thoroly	thoroly	thoroly	thoroly	thoroly	thoroly	thoroly	thoroly	thoroly	thoroly	thoroly
Number of Leachings	2	2	none	none	none	none	none	washed	washed	washed	washed	washed	washed	washed	washed	washed	washed	washed
pH Value of Leachings	4.0-	4.0-																
Alkali Used	NaOH	NaOH	NaOH	NaOH	NaOH	MgO	MgO	NaOH	MgO	NaOH	Ca(OH) ₂	NaOH	NaOH	NaOH	NaOH	Ca(OH) ₂	Ca(OH) ₂	Ca(OH) ₂
Buffer Salt Used, gm.	none	none	none	none	none	none	none	none	Na ₂ SO ₄ -20	none	none	MgSO ₄ -5	none	none	MgSO ₄ -2	none	none	MgSO ₄ -2
Alkali Added to Neutralize Slurry, gm.	none	none	3.5	3.75	3.0	2.5	2.5	none	none	none	none	none	none	none	none	none	none	none
Temperature of Slurry During Alkali Treatment, °F	150-180	75	150-180	150-180	75	150-180	150-180	150-180	150-180	75	75	75	75	180-200	180-200	75	180-200	180-200
Number of Neutral Slurry Leachings	none	none	3	3	3	3	3	none	none	none	none	none	none	none	none	none	none	none
Total Neutral Slurry Filtrate, ml	none	none	1100	1000	1090	1100	1010	none	none	none	none	none	none	none	none	none	none	none
pH Value of Composite Slurry Leachings			6.9	7.1	7.2	7.4	7.0											
Alkali Added to Convert Ferrocyanide, gm.	4.0	4.5	2.5	3.5	3.5	3.0	5.0	6.0	7.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0
Total Alkali Used for Neut. and Extracting, gm.	4.0	4.5	6.0	7.25	6.5	5.5	7.5	6.0	7.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0
Number of Alkaline Slurry Leachings	1	1	1	1	1	1	1	4	4				3	3	3	3	3	3
Total Alkaline Slurry Filtrate, ml	1030	1030	950	1010	960	860	930	2555	2490				2460	2430	2335	2390	2440	2395
pH Value of Composite Alkaline Liquor	9.5	9.6	9.0	9.4	9.6	9.2	9.4	9.3	10.0	10.6	11.2	10.0	10.2	10.0	10.0	10.2	10.2	10.0
Elapsed Time for Entire Test, hrs.	48	48	48	48	48	48	48	48	48	72	72	72	8 da.	8 da.	8 da.	8 da.	8 da.	8 da.
Appearance of Alkaline Liquor	turbid	clear	clear	turbid	clear	clear	clear											
Effect of Boiling Liquor with Acetic Acid	ppt.	turbid	clear	ppt.	clear	clear	clear											
H ₂ S and Sulphide Test on Acidified Liquor	strong	trace	trace	strong	trace	trace	trace						trace	strong	trace	trace	strong	trace
% by Wt. of (CN) ₂ as CNS in Leaching Liquors	0.22	0.23	0.25	0.26	0.25	0.25	0.27											
" " " " " " " " Alkaline Extract	0.03	0.04	0.03	0.03	0.03	0.03	0.03	.065	.135	.067		.060	.025	.026	.027	.025	.028	.028
Total % by Wt. (CN) ₂ as CNS in Extracting Liquors	0.25	0.27	0.28	0.29	0.28	0.28	0.30											
% by Wt. of (CN) ₂ as Fe(CN) ₆ in Alkaline Extract	0.64	0.70	0.47	0.66	0.60	0.22	0.19	.36	.09	.44	.23	.35	.420	.386	.395	.380	.410	.395
" " " " " " " " Remaining in Sludge	0.23	0.13	0.36	0.13	0.22	0.52	0.50	nil	.20	nil	.21	.09	.018	.042	.021	.020	.017	.032
Total % by Wt. of (CN) ₂ as Fe(CN) ₆ in Oxide Matl.	0.87	0.83	0.83	0.79	0.82	0.74	0.69	.36	.290	.44	.44	.44	.438	.428	.416	.400	.427	.427
Grand Total % by Wt. all (CN) ₂ as CNS and Fe(CN) ₆	1.12	1.10	1.11	1.08	1.10	1.02	0.99	.425	.425									
% of (CN) ₂ as CNS Recovered in Alkaline Extract	3.3	4.6	3.5	3.7	3.5	3.9	4.2	15.3	31.8									
% of (CN) ₂ as Fe(CN) ₆ " " " "	71.1	80.4	54.6	80.5	70.6	28.6	26.4	84.7	21.2									
% of (CN) ₂ as Fe(CN) ₆ Remaining in Sludge	25.6	15.0	41.9	15.8	25.9	67.5	69.4	nil	47.0									
% Recovery of Fe(CN) ₆	73.5	84.3	56.6	83.6	73.2	29.8	27.7	100	31.1	100	52	80	95.8	90.2	95.0	95.0	95.9	92.5

TABLE III

TABLE III

Series No.	Q				R				S				T				U				V				W				X				Y				Z																									
Test No.	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65															
Materials:	100				100				100				100				100				100				100				100				100				100				100																					
Spent Oxide, gm.	Ca(OH) ₂				Ca(OH) ₂				Ca(OH) ₂				Ca(OH) ₂				Ca(OH) ₂				Ca(OH) ₂				Ca(OH) ₂				Ca(OH) ₂				Ca(OH) ₂				Ca(OH) ₂				Ca(OH) ₂																					
Alkali, Type	1.0				2.0				3.0				4.0				1.0				2.0				3.0				4.0				1.0				2.0				3.0				4.0				3.0													
Alkali, gm.	2.0				3.0				4.0				5.0				.75				1.0				2.0				3.0				4.0				1.0				2.0				3.0				4.0				3.0									
Buffer Salt, Type	none				Na ₂ SO ₄				none				none				none				none				Na ₂ SO ₄				none				Na ₂ SO ₄				Na ₂ SO ₄				Na ₂ SO ₄				Na ₂ SO ₄				Na ₂ SO ₄													
Buffer Salt, gm.	none				5.0				5.0				5.0				5.0				5.0				5.0				5.0				5.0				2.0				2.0				2.0				0.0				0.0									
1st Leaching.	500				500				500				500				500				500				500				500				500				500				500				500				620													
Water Added, ml.	6				6				6				6				6				6				6				6				6				6				6				6				6													
Time Interval, Days	350				345				342				330				353				337				340				330				365				326				363				352				345				330				432					
Filtrate, ml.	7.3				8.9				10.0				10.2				7.6				9.0				10.3				10.6				7.7				8.0				10.2				10.4				10.6				10.8				8.1					
pH Value	C				C				C				T				C				C				C				T				C				C				C				ST				T				PS				C					
Appearance	C				C				C				T				C				C				C				T				C				C				C				C				C				C				C					
2nd Leaching.	500				500				500				500				500				500				500				500				500				500				500				500				500													
Water Added, ml.	1				1				1				1				1				1				1				1				1				1				1				1				1													
Time Interval, Days	465				450				455				452				440				438				454				443				490				485				495				495				507				488				482					
Filtrate, ml.	7.3				8.8				10.1				10.2				7.3				8.7				9.9				10.3				10.2				10.2				10.2				10.2				10.2				10.2				10.2					
pH Value	C				C				C				C				C				C				C				C				C				C				C				C				C				C									
Appearance	C				C				C				C				C				C				C				C				C				C				C				C				C				C									
3rd Leaching.	500				500				500				500				500				500				500				500				500				500				500				500				500													
Water Added, ml.	1				1				1				1				1				1				1				1				1				1				1				1				1													
Time Interval, Days	432				430				430				390				420				413				420				385				499				513				480				457				470				460				520					
Filtrate, ml.	7.3				8.7				10.1				10.2				7.3				8.5				10.1				10.2				10.2				10.2				10.2				10.2				10.2				10.2				10.2					
pH Value	C				C				C				C				C				C				C				C				C				C				C				C				C				C									
Appearance	C				C				C				C				C				C				C				C				C				C				C				C				C				C									
4th Leaching.	500				500				500				500				500				500				500				500				500				500				500				500				500													
Water Added, ml.	1				1				1				1				1				1				1				1				1				1				1				1				1													
Time Interval, Days	387				446				397				376				423				423				426				398				465				462				457				460				407				468				436					
Filtrate, ml.	7.3				8.6				10.1				10.2				7.4				8.4				10.1				10.2				7.7				7.9				10.1				10.2				10.2				10.4				7.8					
pH Value	C				C				C				C				C				C				C				C				C				C				C				C				C				C									
5th Leaching.	1634				1671				1624				1548				1636				1611				1640				1556				1766				1807				1799				1775				1737				1771				1803					
Total Filtrate, ml.	1634				1671				1624				1548				1636				1611				1640				1556				1766				1807				1799				1775				1737				1771				1803					
pH Value	10.1				10.1				10.1				10.1				10.1				10.1				10.1				10.1				10.1				10.1				10.1				10.1				10.1				10.1									
% by wt. (CN) ₂ Extracted	.037				.239				.281				.297				.043				.236				.314				.316				.222				.336				.453				.450				.448				.450				.232					
as Fe(CN) ₆	.094				.14				.18				.20				.09				.15				.17				.105				.035				.038				.090				.094				.093				.105				.038					
as CNS	.094				.14				.18				.20				.09				.15				.17				.105				.035				.038				.090				.094				.093				.105				.038					
% by wt. (CN) ₂ in Original Oxide	.328				.328				.328				.328				.328				.328				.328				.328				.328				.328				.328				.328				.328													
as Fe(CN) ₆	.328				.328				.328				.328				.328				.328				.328				.328				.328				.328				.328				.328				.328													
as CNS, by Simple Leaching	.328				.328				.328				.328				.328				.328				.328				.328				.328				.328				.328				.328				.328													
as CNS, by KOH Extraction	.328				.328				.328				.328				.328				.328				.328				.328				.328				.328				.328				.328				.328													
% Recovery for Fe(CN) ₆	11				73				86				91				13				72				96				96				48				72				97				97				96				97				50					
Times Excess of Theoretical	28.6				8.8				11.2				14.2				24.4				8.9				10.1				13.3				3.6				3.1				4.6				7.0				9.4				11.7				3.4					
Ca(OH) ₂ Consumed	28.6				8.8				11.2				14.2				24.4				8.9				10.1				13.3				3.6				3.1				4.6				7.0				9.4				11.7				3.4					
on Basis of Total Ca(OH) ₂ Added	28.6				8.8				11.2				14.2				24.4				8.9				10.1				13.3				3.6				3.1				4.6				7.0				9.4				11.7				3.4					
on Basis of Each Ca(OH) ₂ Charge	28.6				8.8				11.2				14.2				24.4				8.9				10.1				13.3				3.6				3.1				4.6				7.0				9.4				11.7				3.4					