

ACID LEACHING OF NICKEL
FROM DUNITE ROCK

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ABSTRACT.

It has been known for some time ¹ that the major component of Dun Mountain dunite (an almost pure olivine rock $(\text{Mg,Fe,Ni})_2\text{SiO}_4$) is soluble in dilute mineral acids. However, the cost of reagents rules out an acid dissolution process as a source of nickel. Also the presence of large amounts of iron in a dilute nickel solution would introduce technological difficulties and adverse economic factors in the separation of these metals. Any efficient acid leaching process would need to selectively remove the nickel from the lattice in preference to magnesium and (particularly) iron. Such a requirement may be met if a secondary, essentially solid phase reaction took place in which cations in the lattice are substituted by protons without loss of lattice structure. Some experimental support for such a reaction has been forthcoming ^{2,3} and the object of this research was an investigation into this lattice theory as well as a general review of the behaviour of dunite under the action of various acid leaching agents.

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CHAPTER ONE

GENERAL REVIEW.

1.1. THE MAJOR SOURCES OF NICKEL

Commercial nickel deposits are of two basic types - the sulphide ores (about 4 - 12% nickel) and the oxide or lateritic ores (0.5 - 4.0% nickel) - although both are derived from the same rock types. The nickel bearing rocks are those rich in magnesium and iron ("mafic"), and of these the most important is peridotite, with the norite variety of gabbro of secondary importance.

TABLE 1. Average chemical composition of Peridotite and Gabbro. ⁴

	% Nickel	% Iron Oxide plus Magnesia	% Silica plus Alumina
Peridotite	0.20	43.3	45.9
Gabbro	0.016	16.6	66.6

In both peridotite and gabbro the most important constituent mineral is olivine. Because of the similar size of divalent nickel, iron, and magnesium ions (ionic radii 0.78, 0.75, 0.65 Å respectively) it is thermodynamically feasible for the nickel to substitute for either or both iron and magnesium in the crystal lattice.

As yet, such mafic rocks are unsuitable for economic nickel extraction but there exist naturally occurring processes whereby nickel is accumulated within certain minerals and from these nickel may be extracted on an economic basis:

(i) Sulphidization - accumulation as the sulphide - the mechanism of this mode of formation is the subject of some debate. 5,6

(ii) Decomposition and Weathering - the formation of laterites, which is very common in temperate to tropical areas.

1.2 MINERALOGY OF NICKEL SOURCES.

Of the known nickel minerals Pentlandite $(\text{Ni,Fe})_9 \text{S}_8$ and Nickeliferous pyrrhotite $(\text{Ni,Fe})_7 \text{S}_8$ are of main economic importance. Sulphide ores are readily concentrated by conventional techniques such as classification, flotation and magnetic separation. The simple mining and extraction processes applicable to nickel sulphide ores are major reasons why these ores account for nearly 75% of nickel production whereas they make up only 25% of the known nickel deposits.

The process of laterization by weathering involves dissolution of the nickel and magnesium and precipitation of iron close to the ground surface. Under favourable conditions the solutions rich in nickel will be accumulated and the nickel may be taken up into the crystal lattice of some host mineral.

Because of their mode of formation lateritic deposits vary much more widely in their chemical and mineral content than sulphide deposits. Not only is the nickel content lower but there are larger and more diverse amounts of unwanted materials.

1.3 THE EXTRACTIVE METALLURGY OF NICKEL.

There are two basic approaches to extraction, namely pyrometallurgy and hydrometallurgy. Pyrometallurgy involves heating the ore or ore concentrate in such a way as to concentrate the nickel and eliminate some of the unwanted constituents as slag or escaping volatiles. Hydrometallurgy involves heating a slurry of the ore with a suitable leaching liquor in such a way as to solubilize and extract the entrained nickel. There has been increasing interest in this latter process in recent years due to its relatively low pollution factor.

(a) Pyrometallurgy of sulphide ores.

This multistep process depends initially upon the varying stabilities of metal sulphides in relation to the respective metal oxides. After most of the iron has been oxidized the nickel calcine is smelted in the presence of a suitable siliceous flux to separate the remaining iron as a silicate slag. The resultant "converter matte" is purified by subsequent pyrometallurgical or hydrometallurgical steps.

(b) Hydrometallurgical Techniques.

The major commercial, purely hydrometallurgical, process is that of the Sherritt Gordon Mines Ltd. ⁷

This process involves dissolution of the nickel ores in an oxygenated ammonia solution. The nickel, cobalt, and copper are solubilized as the ammine complexes. Under the operating conditions iron does not form a stable ammine complex but is precipitated as ferric oxide. Nickel can readily be recovered from ammoniacal solutions by reduction with hydrogen at high temperatures and pressures.

Other "hydrometallurgical" processes involve an initial pyrometallurgical step in which the sulphur is eliminated by roasting. The calcine is then selectively reduced by a carbon dioxide/carbon monoxide mixture. The nickel is recovered from the kiln product by leaching with ammonia in the presence of oxygen under controlled redox conditions.

(c) Treatment of Lateritic Ores.

There are four main technological problems associated with extraction of nickel from laterites:

- (i) low nickel content and hence excessive tonnages of ore to be treated,
- (ii) the impossibility of upgrading the ore by physical means to a concentrate because of the lack of any definite nickel bearing minerals,
- (iii) variability of mineral, and hence chemical content, thus requiring a technique which does not demand a rigid feed analysis, and
- (iv) high water content, both free and chemically bound, which may be up to 40% of the total ore weight.

To date four basic techniques have been used to treat nickel laterites: (1) smelting in the presence of a

sulphur containing compound to produce nickel matte, (2) smelting to ferro-nickel, (3) sulphuric acid leaching, and (4) reduction followed by ammonia leaching. Of these only sulphuric acid leaching is a purely hydrometallurgical process but it can only be employed in the absence of large amounts of silica and magnesia. Although nickel may be extracted from such a laterite, large quantities of iron will go into solution as the soluble sulphate. That is, the reaction is non-selective. This creates two major problems; firstly, the amount of acid consumed is disproportionately high and secondly, it is extremely difficult to recover nickel from a concentrated iron solution. Normally the iron would have to be precipitated as the insoluble hydroxide before the nickel could be recovered. The corrosive nature of the leach liquor (especially when used at high temperatures and pressures) introduces significant engineering problems also. This leaching process is employed in the Moa Bay Mining Co. process for nickel treatment.⁸

1.4 RECENT RESEARCH ON LEACHING OF METAL ORES

(a) Aqueous Leaching. Aqueous leaching of raw ore finds little commercial application as the process, which is somewhat analogous to the natural weathering of laterites and serpentines, is very slow and metal recoveries are generally low.^{9,10}

Despite this, aqueous leaching of nickel ore may find some application in specific localized areas if nickel is present in a readily soluble form. If, however, the ore

is given some preliminary treatment so as to convert it into a form of high solubility e.g. metal chloride, oxychloride, sulphate etc. aqueous leaching may (sometimes) be used. Chlorination ¹¹⁻¹³ has been proposed for this conversion, after which the ore may be leached with hot water. A Polish patent ¹⁴ suggests the use of slags, wastes and other materials containing 0.15 - 0.5% nickel in a similar process. The nickel materials are roasted with sulphur-containing foundry wastes such as FeS_2 , FeS , FeSO_4 , CaSO_4 etc., after which the soluble nickel sulphates may be leached with water or dilute acid.

(b) Alkaline Leaching. Basic leaching agents consist of ammonia, ethanolamine, ethylenediamine, etc. and their derivatives. These form soluble complexes with several metals, notably copper, cobalt, nickel, zinc and cadmium. Most ammonia leaching processes are modifications of the process of Professor M.H. Caron ¹⁵⁻¹⁷ described above as the process of Sherritt Gordon Mines Ltd. Caustic soda has been proposed as a leaching agent by Russian ^{18,19} and Japanese ²⁰ workers to recover nickel, cobalt and arsenic from ores.

(c) Acid Leaching. Many workers have investigated the process of sulphuric acid leaching of nickel ores and concentrates. ²¹⁻²⁴ Antier ²⁵ proposes sulphuric acid treatment of pulped silicate ores and suggests that the filtrate be dried and oxidatively roasted to dehydrate the sulphates - ferric sulphate is then insoluble and may be separated by washing. Greene ^{26,27} discusses a serpentine ore which he suggests may be treated by carbon-monoxide reduction and sulphuric acid leaching. Japanese patents ^{28,29}

involve a reductive roast followed by dilute sulphuric acid leaching. All of these latter processes have yet to find industrial application.

Hydrochloric acid leaching has had limited application possibly due to its cost. The most important chemical disadvantage of chloride systems is that most metals go into solution and hence the complexity of separation is increased.³⁰ Chloride solutions are also highly corrosive toward traditional plant materials such as stainless steel, titanium and lead. Pawel³¹ proposed hydrochloric acid leaching of an oxidized low grade nickel ore followed by neutralization of the nickel/magnesium/iron chloride liquor with magnesium oxide. After selective precipitation of the iron and nickel as hydroxides the magnesium chloride solution is filtered, evaporated and decomposed thermally to regenerate hydrogen chloride and magnesium oxide. Hydrochloric acid has also found some limited application in leaching nickel mattes.^{32,33} Urazov and Bogatsky³⁴ conducted laboratory experiments into the efficiency of various leachants towards complex iron and nickel ores. Their conclusion (in the case of the nickel rich Akkerman ores) was that nitric acid is less efficient than either hydrochloric or sulphuric acids.

Sulphurous acid has also been suggested as a leachant for oxidized low grade nickel ores.^{35,36} Nickel and cobalt are reduced to the metallic state (usually by a hydrogen/carbon monoxide mixture) prior to leaching. The suggested method of nickel and cobalt recovery is precipitation by hydrogen sulphide gas from the pregnant solution.

(d) Leaching with Iron Salts. Iron salts have found some application in leaching nickel from ores and mattes.³⁴ Russian workers³⁷ have concluded that extraction of nickel from ores of the Serov region is better (22%) when using ferrous salts than sulphuric acid (10.7%). The use of ferric chloride has been investigated by Kryukova³⁸ who was able to selectively precipitate nickel and cobalt. Greene²⁶ has proposed a process for leaching nickel and cobalt from roasted reduced ores by leaching with ferric sulphate at a pH higher than the range at which sulphuric acid is effective.

1.5 RESEARCH ON LEACHING OF OLIVINE.

Considering the wealth of literature available concerning the treatment of the economic ores of nickel, the investigation of their parent rock, olivine, appears sadly neglected. Hanzo Mase and colleagues have examined the behaviour of olivine and its metamorphosised derivative serpentine under the action of sulphuric acid³⁹ and chelating agents.⁴⁰ Calcination of olivine was also undertaken⁴¹ to determine its suitability as a fertilizer. Weiskirchner⁴² has also studied the behaviour of olivine at high temperatures. The only studies of olivine related to its low mineral content have been those of Mase⁴⁰ and Zucchini^{43,44} who examined the acid solubility of olivine and the possibility of selective leaching of cations from the lattice. Other areas of interest have involved the magnesium content either as a fertilizer⁴¹ or as a source of magnesium chloride (by chlorination).⁴⁵ Sanemasa, Yoshida, and Ozawa⁴⁶ in a recent publication

reported a study of the dissolution of olivine in various aqueous acids. Their conclusion was that there is no selective dissolution of component metals under the action of the various acids employed.

1.6 NICKEL CONTENT OF OLIVINE AND DUNITE.

Dunite is a hard, relatively unjointed, igneous rock. The major component of dunite is olivine, a greenish-yellow mineral of varying composition, with a small amount of accessory chromite. The chromite (about 2½% by weight) is in the form of the mineral picotite. The composition of the olivines varies from forsterite (Mg_2SiO_4), designated Fo, to fayalite (Fe_2SiO_4), Fa. Magnesium-rich olivines are common constituents of ultrabasic and basic rocks. The iron-rich members crystallize in small quantities in some acid and alkaline plutonic and volcanic rocks. At the magnesium-rich end of the series chromium and nickel (usually in small amounts) are present. The Dun Mountain dunite studied in this project is a $Fo_{90} Fa_{10}$ solution containing approximately 0.3% nickel.

Investigations by Nishimura, Yagi, and Yamamoto ⁴⁷ clearly demonstrated a decrease in the nickel/magnesium ratio with decreasing magnesium content in olivines. Numerous explanations have been proposed for this decrease. On the basis of phase relationships in the binary systems $Mg_2SiO_4 - Fe_2SiO_4$ (Bowen and Schairer ⁴⁸) and $Ni_2SiO_4 - Mg_2SiO_4$ (Ringwood ⁴⁹) a complete series of solid solutions is expected. Also in the ternary system ($Mg_2SiO_4 - Fe_2SiO_4 - Ni_2SiO_4$) Ni_2SiO_4 lies between the other two in its melting point and it is difficult from these

observations to explain why nickel content decreases abruptly with the decrease of forsterite. Ringwood attributed the behaviour of nickel to preferential replacement of nickel ions by iron ions in the olivine structure. More recently Burns and Fyfe ⁵⁰ have proposed a rationale in terms of the crystal field stabilization energy for transition metal ions.

1.7 THE STRUCTURE OF OLIVINE. ⁵¹

The unit cell dimensions for olivine are:-

$$a = 4.755 \overset{\circ}{\text{A}}, b = 10.21 \overset{\circ}{\text{A}}, c = 5.985 \overset{\circ}{\text{A}} .$$

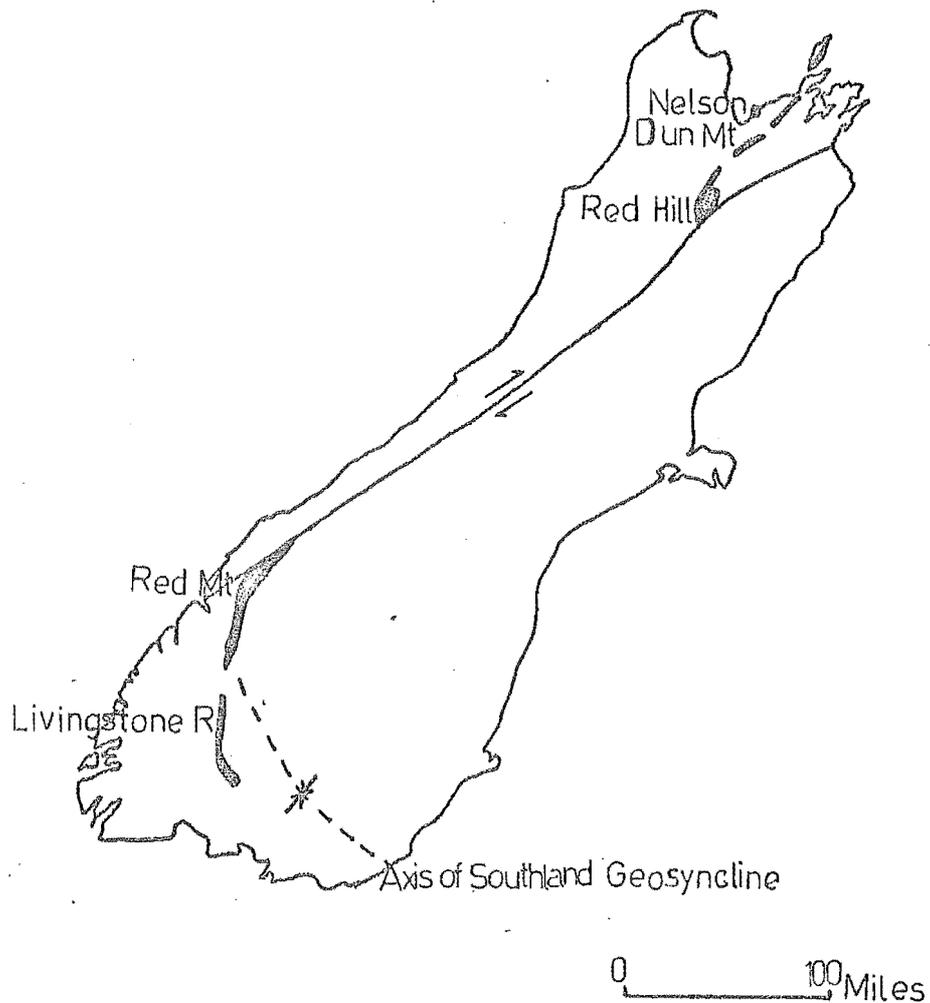
The structure consists of individual silicon-oxygen tetrahedra linked by magnesium atoms each of which has six nearest neighbour oxygens. These oxygen atoms lie in sheets parallel to the (100) plane and are arranged in approximate hexagonal close packing. In accordance with full orthorhombic symmetry the silicon-oxygen tetrahedra point alternately either way along the x and y axes. The magnesium atoms do not occupy one set of equivalent lattice positions; half are located at centres of symmetry and half on reflection planes, the former having as nearest neighbours two oxygen atoms from two adjacent tetrahedra, the latter, two oxygen atoms from one adjacent tetrahedron.

1.8 GEOLOGY AND GEOGRAPHY OF DUNITE ORES IN NEW ZEALAND.

A comprehensive study of the availability and mining potential of dunite rock in New Zealand has been

FIGURE 1.

Location of South Island Dunite Orebodies.



Abstracted from the Geological Map of New Zealand
N.Z.D.S.I.R. 1957

undertaken by Billingham and Nicholson ⁵² in connection with the setting up of a local fertilizer industry. The fertilizer process described in their report involves treatment of a mixture of Nauruan phosphate and New Zealand dunite and a comprehensive costing of the New Zealand raw material is set out. Although now somewhat out of date, the report discusses the various sources of dunite in New Zealand, the availability of labour, transport, and electric power, and the economic factors involved in the supply of large tonnages of crushed ore.

Major orebodies in New Zealand are made up of ultramafic rock containing a central core of relatively un-serpentinized dunite, harzburgite and pyroxene, surrounded by a margin of serpentine. The other smaller bodies (in North Auckland and West Coast-Fiordland) are almost completely serpentinized ultramafic bodies found in Cretaceous and Tertiary rocks. The thickness is extremely variable in all districts and the lenses vary from a few tens to a few hundreds of feet in width. In a few places the lenses broaden out into roughly circular masses of largely un-serpentinized rock, two to six miles in width.

1.9 MAJOR OCCURRENCES OF DUNITE IN NEW ZEALAND.

(a) Dun Mountain. Situated seven miles south east of Nelson, Dun Mountain has a roughly circular core approximately two by two and a half miles in size elongated

in a north-easterly direction. It is surrounded by a wide margin of sheared and serpentized ultramafic rock, the widest band of serpentine being associated with a large fault on the western margin. The mountains and spurs to the north-west are composed of dunite and harzburgite with minor pyroxenites.

(b) Red Hills - Wairau Valley. In this intrusion, ultramafic rocks are exposed over a forty-two square mile area. Red Hill rises 6,000 feet from the fault scarp marking the southern boundary of ultramafic rocks, so the vertical section through the mass is 4,000 feet.

(c) Red Mountain - North-West Otago. This body lies in a very inaccessible area in the Livingstone Range. Red Mountain itself lies at the southern end of the northern lens in Otago. Geology is similar to the Dun Mt. area, however deformation and serpentization are much more intense.

1.10 ECONOMIC LIMITATIONS OF THE PROJECT.

The factor of economics is not generally encountered in post graduate projects and its introduction here somewhat limited the types of processes and reagents which could seriously be considered. As may be gathered by reference to Table II (Analysis of Dun Mt. dunite) the nickel content is too low for consideration of conventional extraction procedures but the possibility of establishing a cyclic hydrometallurgical process to treat the ore for its own sake or, perhaps more

realistically, establishment of an economic side reaction to its known fertilizer potential cannot be discounted. Despite this restriction processes were considered which would be theoretically outside the limitations of current plant operation e.g. the use of organic chelating agents which would severely strain the profitability of anything but a highly efficient cyclic and regenerative industrial process.

TABLE II - Chemical and Modal Composition of Dunite
from Dun Mountain, Nelson 53.

Olivine	97.5%	SiO ₂	39.53
Chromite (Chromian Spinel)	2.5%	Al ₂ O ₃	0.93
Chromian Diopside (Tr.)		Fe ₂ O ₃	0.65
Serpentine (Tr.)		FeO	7.62
	<hr/>	MgO	48.83
	100.0%	CaO	tr.
		Na ₂ O	tr.
		H ₂ O+	0.89
		H ₂ O-	0.16
		TiO ₂	0.013
		MnO	0.12
		CO ₂	0.06
		S	tr.
		NiO	0.32
		Cr ₂ O ₃	1.01
		CoO	0.018
		<hr/>	
			100.15%

CHAPTER TWO

EXPERIMENTAL AND RESULTS

2.1 APPARATUS AND MATERIALS.

The leaching reactions were studied in a 150 ml jacketed cell thermostated to a constant temperature of either 30°C. or 40°C. Initially the olivine sample was crushed to a mesh size less than 12. As the effect of particle size became more apparent this ore was divided into six further samples.

- (1) Less than mesh 60 (250 μ)
- (2) Mesh 60 to mesh 45 (350 μ)
- (3) Mesh 45 to mesh 30 (500 μ)
- (4) Mesh 30 to mesh 25 (710 μ)
- (5) Mesh 25 to mesh 16 (1000 μ)
- (6) Greater than mesh 16.

A mechanical stirrer kept the ore and leaching liquor slurried during reaction. The consumption of acid in the leaching process was determined by the acid titre required to maintain the leaching liquor at a constant pH. Addition of acid was controlled by use of a "Radiometer" automatic titrator (T.T.T. 1c), coupled with a "Titron" combination electrode. The pH meter was calibrated against 0.05 M potassium hydrogen phthalate (pH = 4.00 + 0.0012 °C⁻¹) and potassium tetroxalate (pH = 1.68 + 0.001 °C⁻¹).

Analysis of the dunite leach liquor involved use

of a Techtron AA-5 atomic absorption spectrophotometer. Samples for analysis were drawn off the leaching solution by pipette, centrifuged to remove suspended dunitite powder and analysed by conventional atomic absorption technique i.e. using an oxidizing air/acetylene flame and recommended parameters for lamp current, monochromator setting, and slit width.

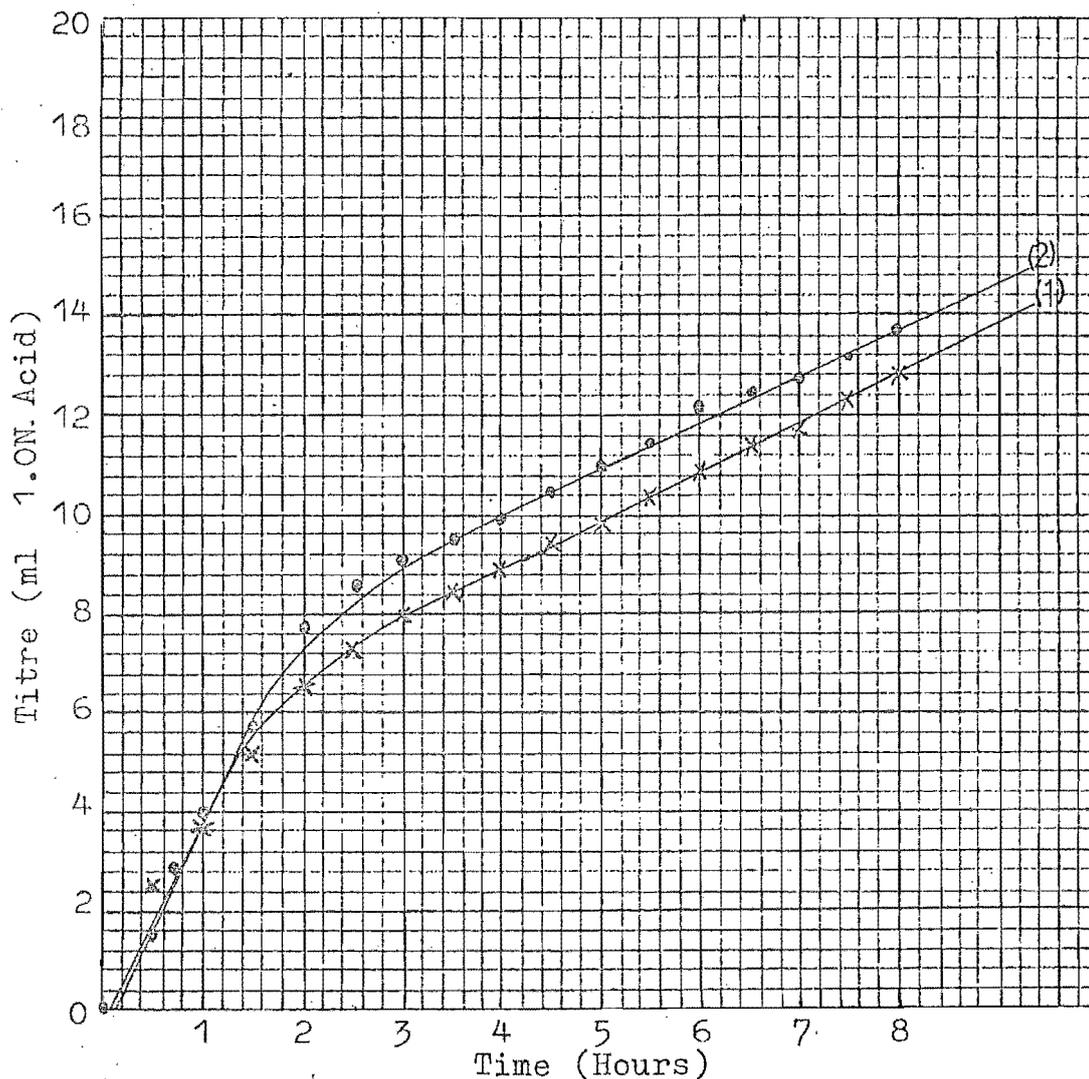
Ferric ion concentrations were determined colourimetrically by the thiocyanate method ⁵⁴ using a Beckman DB-G grating spectrophotometer. Infrared spectra were recorded for nujol mulls using a Shimadzu recording spectrophotometer (IR-127G) and X-ray analyses on a Phillips Debye Scherrer powder camera using a copper target X-ray tube and powdered samples mounted in Lindemann tubes.

Results of all leaching studies are represented graphically on the following pages.

(i) as a plot of acid consumption versus time,
and

(ii) as a plot of nickel or iron concentration in the leach liquor versus time. In each case reaction parameters and instrumentation are noted beneath the graph.

GRAPH 1. Comparison of HCl and H₂SO₄ as leaching agents.



Non-standard conditions:

Dunite grainsize: Less than 12 mesh

Burette Acid concentration: 1.04 N.

pH of leach liquor: 3.0

Temperature: 30 deg. C.

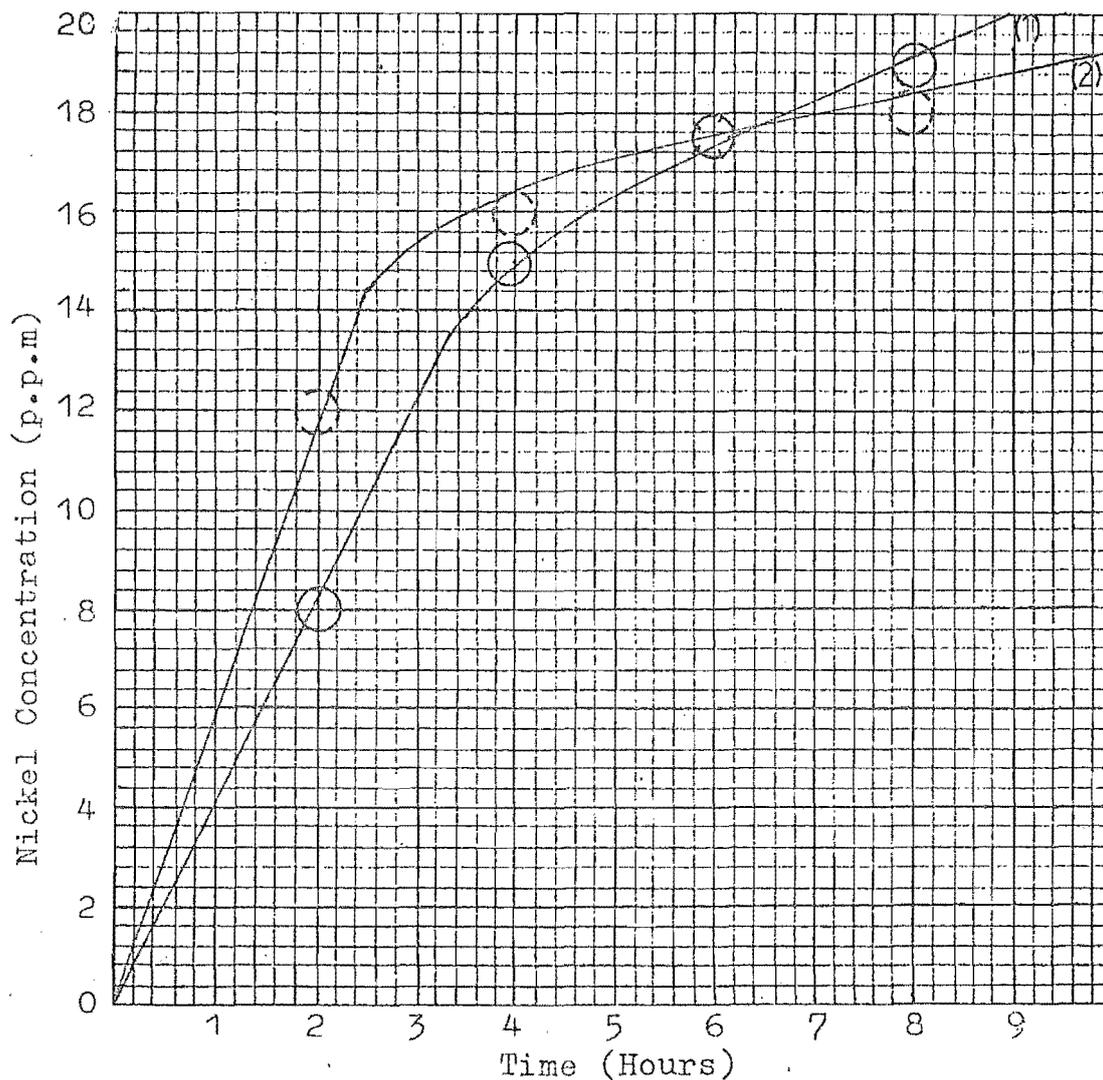
Weight dunite used: 100 g.

Volume of leaching solution: 100 ml

Composition of leach liquor (1) H₂SO₄ (aq.)

(2) HCl (aq.)

GRAPH 2. Analysis of leach liquors of graph 1.



Instrument: Varian Techtron A.A. 5 Atomic
Absorption Spectrophotometer.

Monochromator Setting: 232.0 nm.

Lamp Current: 5 mA.

Slit width: 50 μ .

Standard: Nickel chloride/Ferrous Ammonium Sulphate.

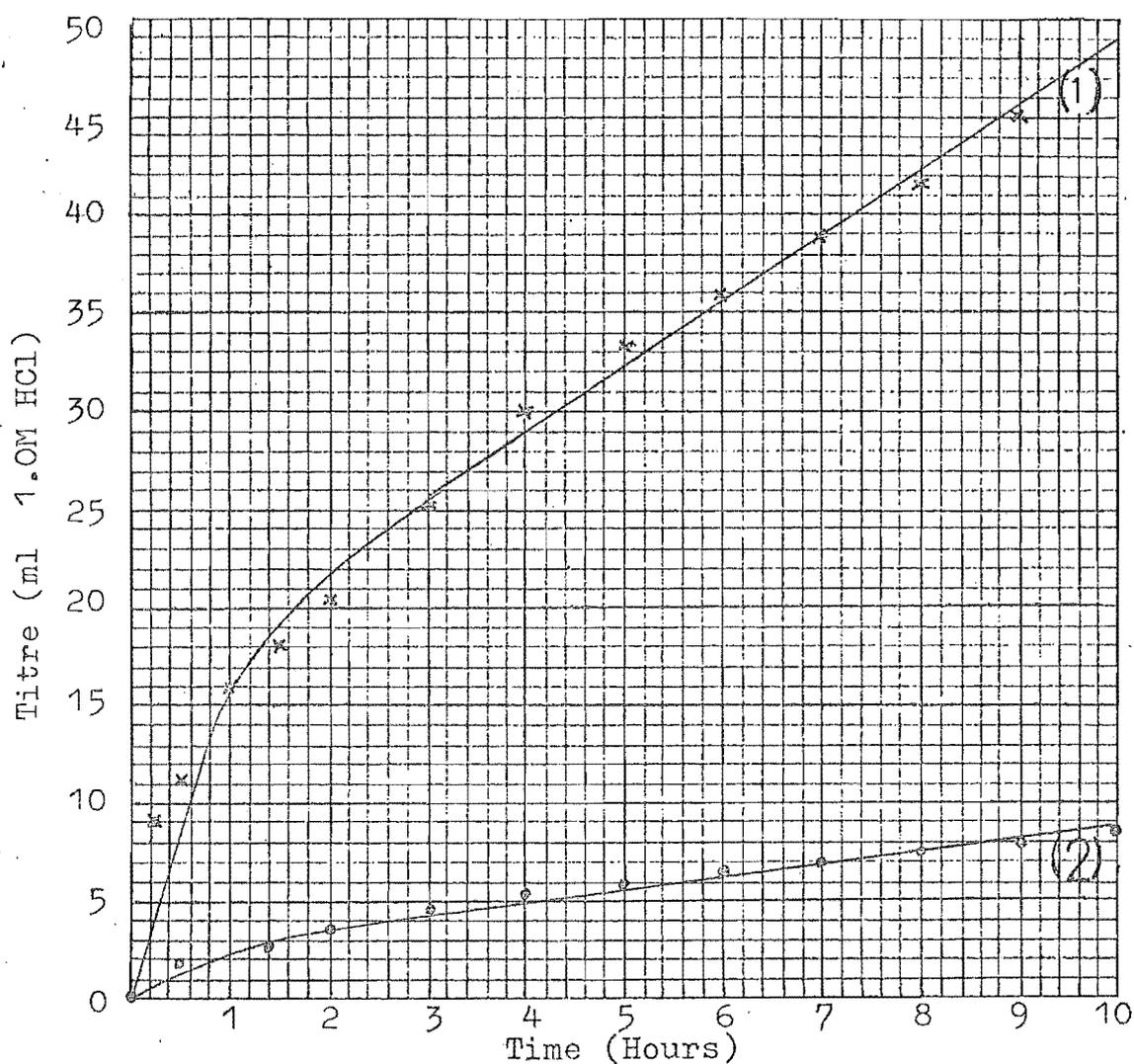
Flame Type: Air/Acetylene

Flame Stoichiometry: Oxidizing

Composition of leach liquor (1) H_2SO_4

(2) HCl

GRAPH 3. Effect of pH on reaction rates



Standard Conditions:

Dunite grainsize: Mesh 45 (350 μ) to mesh 30 (500 μ)

Burette acid concentration: 1.04 M

Temperature: 40 deg. C.

Weight dunite used: 25 grams

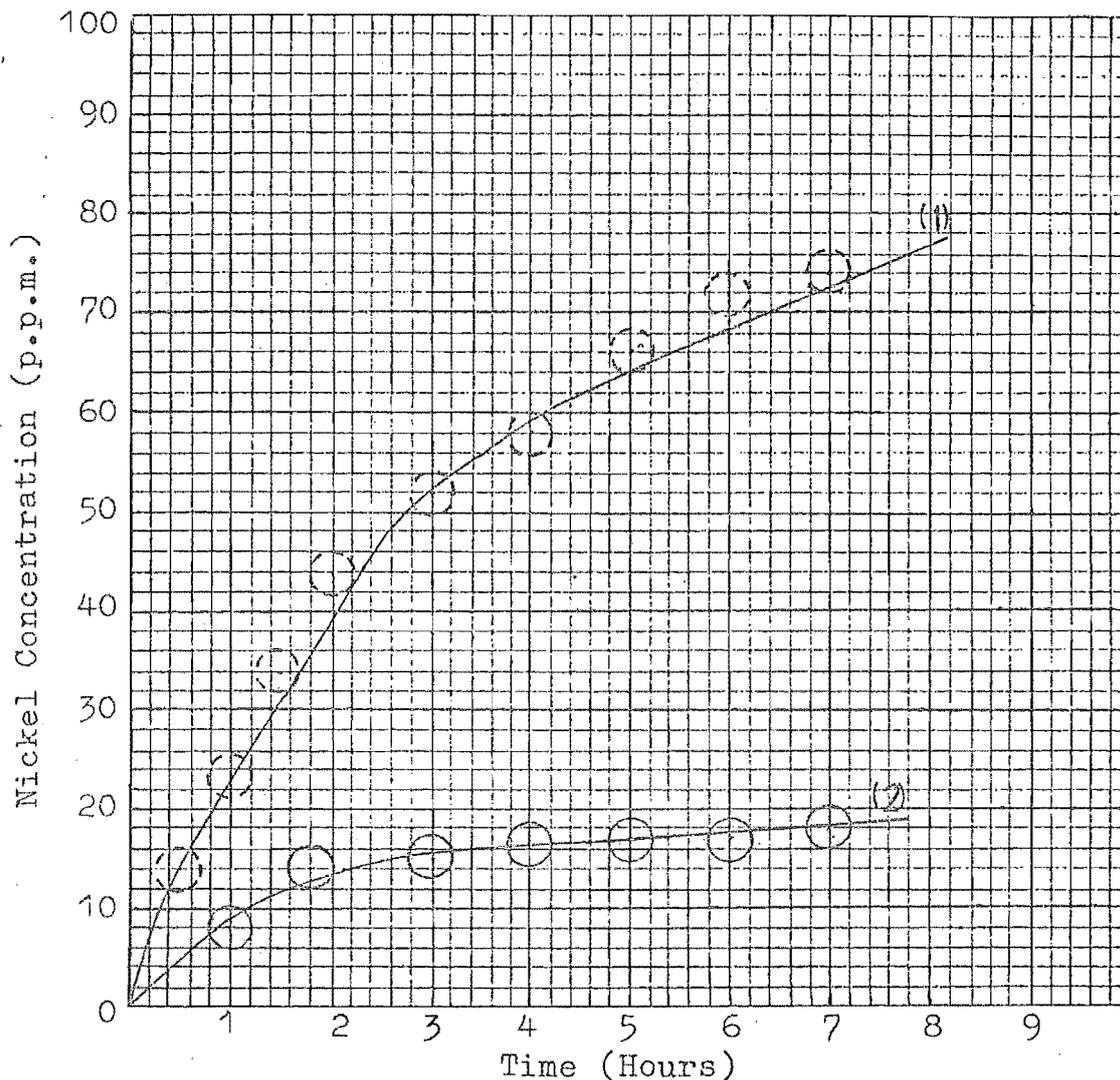
Volume of leaching solution: 75 mls

Composition of leach liquor: Aqueous HCl

pH of leach liquor (1) 1.0

(2) 2.5

GRAPH 4. Analysis of leach liquors of graph 3



Instrument: Varian Techtron A.A.5 Atomic Absorption Spectrophotometer.

Monochromator Setting: 232.0 nm

Lamp current: 5 mA.

Slit width: 50 μ .

Standard: Nickel Chloride/Ferrous Ammonium Sulphate

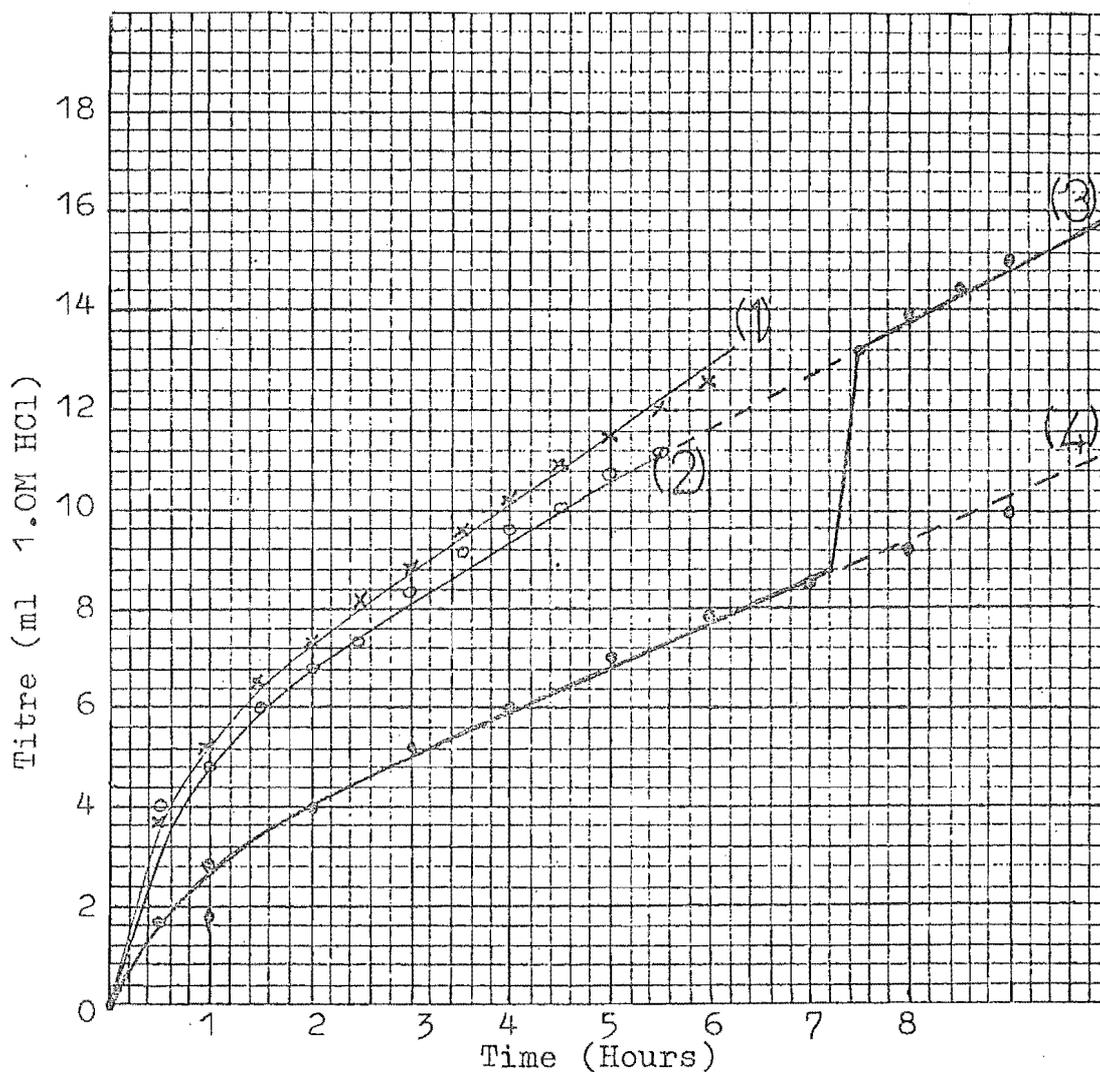
Flame Type: Air/Acetylene

Flame Stoichiometry: Oxidizing

pH of leach liquor (1) 1.0

(2) 2.5

GRAPH 5. Effect of excess metal ion solutions
as leaching agents.

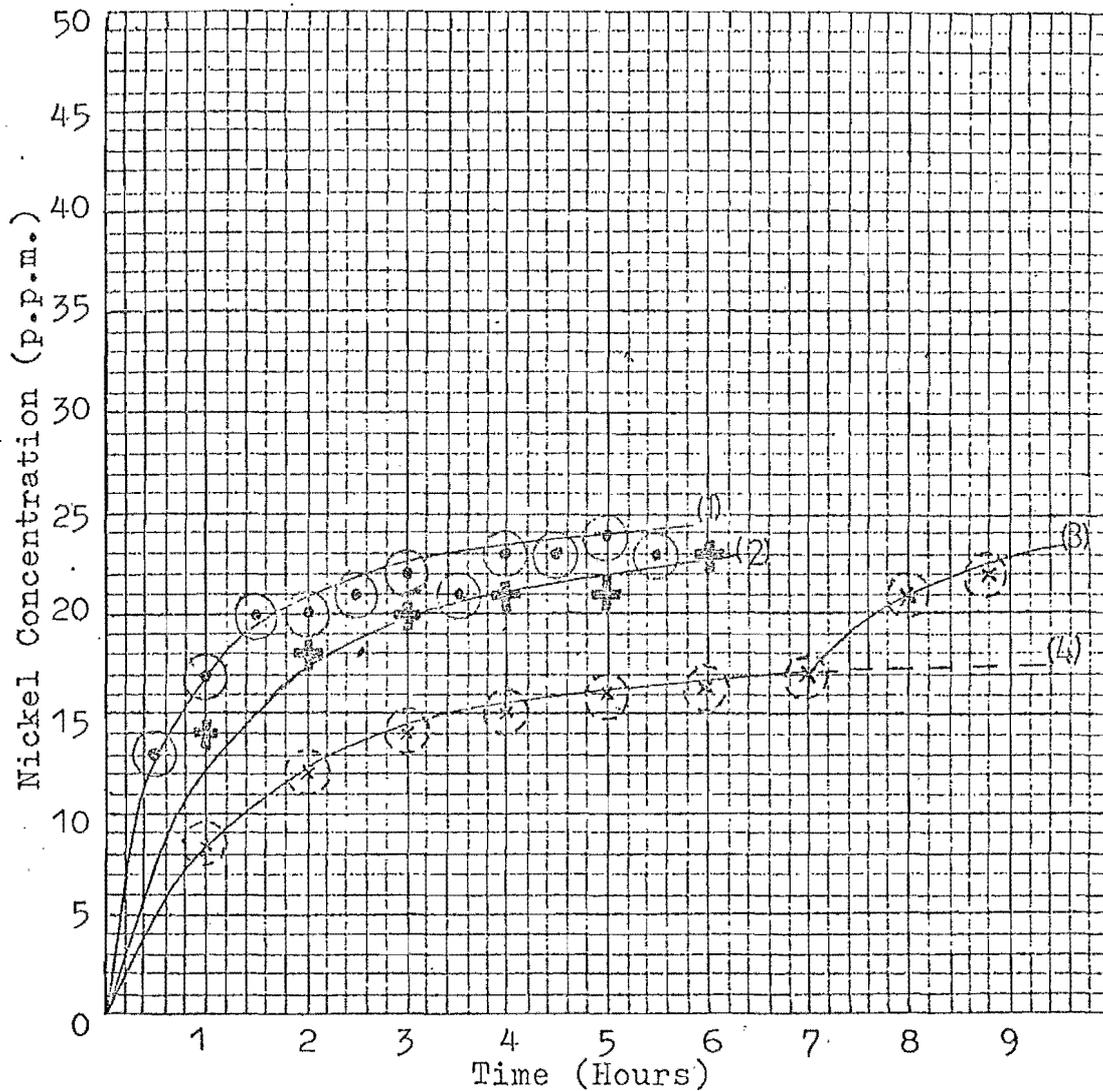


Standard Conditions (As in graph 3)

pH of leach liquor: 2.5.

Composition of leach liquor: (1) Aqueous HCl/Ferrous Ammonium Sulphate (2.75g)
 (2) Aqueous HCl/Magnesium Sulphate (1.71 g)
 (3) Aqueous HCl initially Ferrous Ammonium Sulphate (2.75 g) added at 7.25 hours.
 (4) Aqueous HCl.

GRAPH 6. Analysis of leach liquors of graph 5.



Instrumentation: As in graph 2

Composition of leach liquors (1) Aqueous HCl/Ferrous

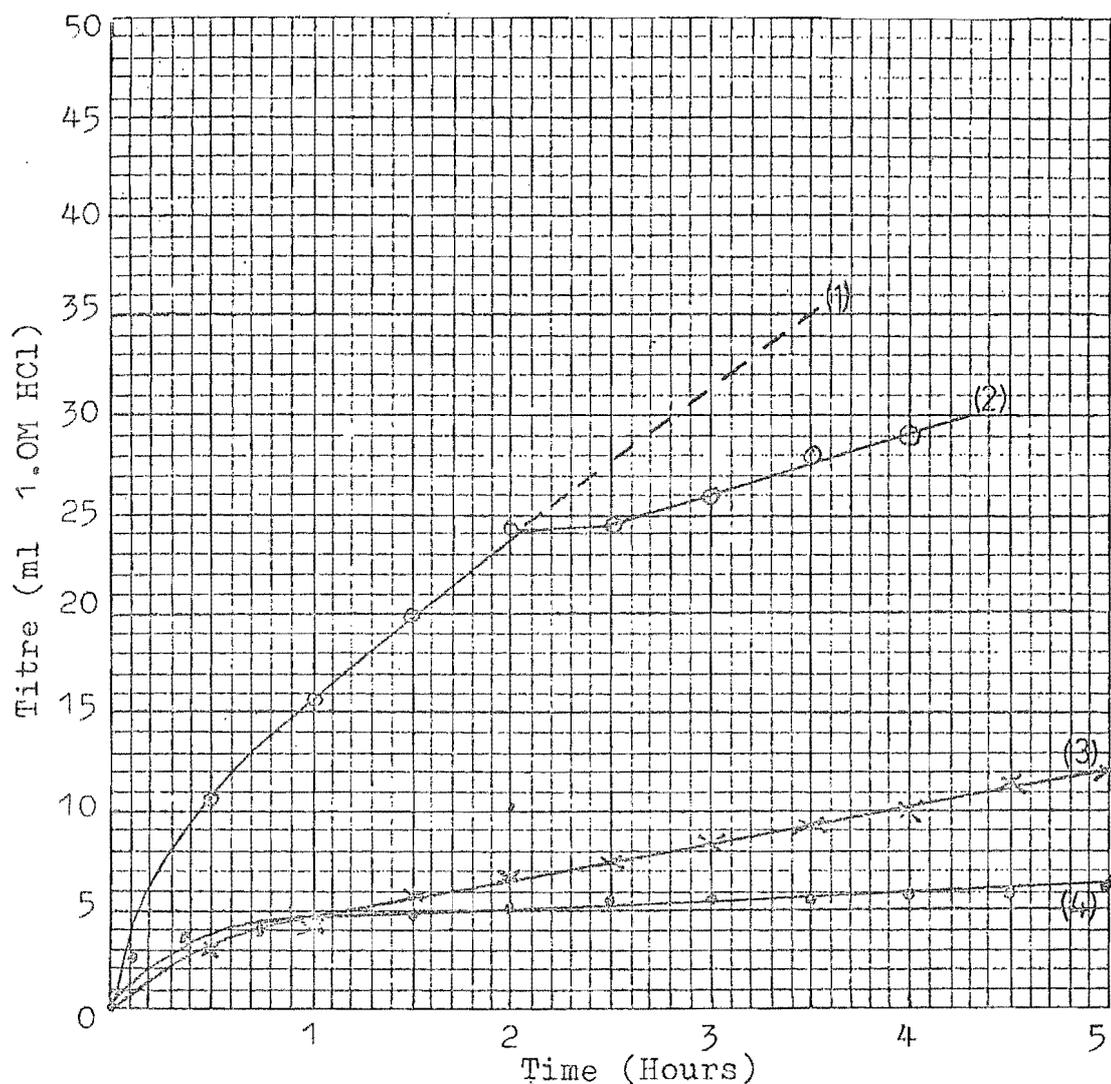
Ammonium Sulphate.

(2) Aqueous HCl/Magnesium Sulphate.

(3) Aqueous HCl initially Ferrous ammonium sulphate added at 7.25 hours.

(4) Aqueous HCl

GRAPH 7. Effect of ferric ion as a leaching agent.



Non-standard conditions (As in graph 1)

Composition of leach liquor (1) Aqueous HCl

(2) Aqueous HCl initially $\text{Fe}_2(\text{SO}_4)_3$ (3 g) added after two hours

(3) Aqueous HCl

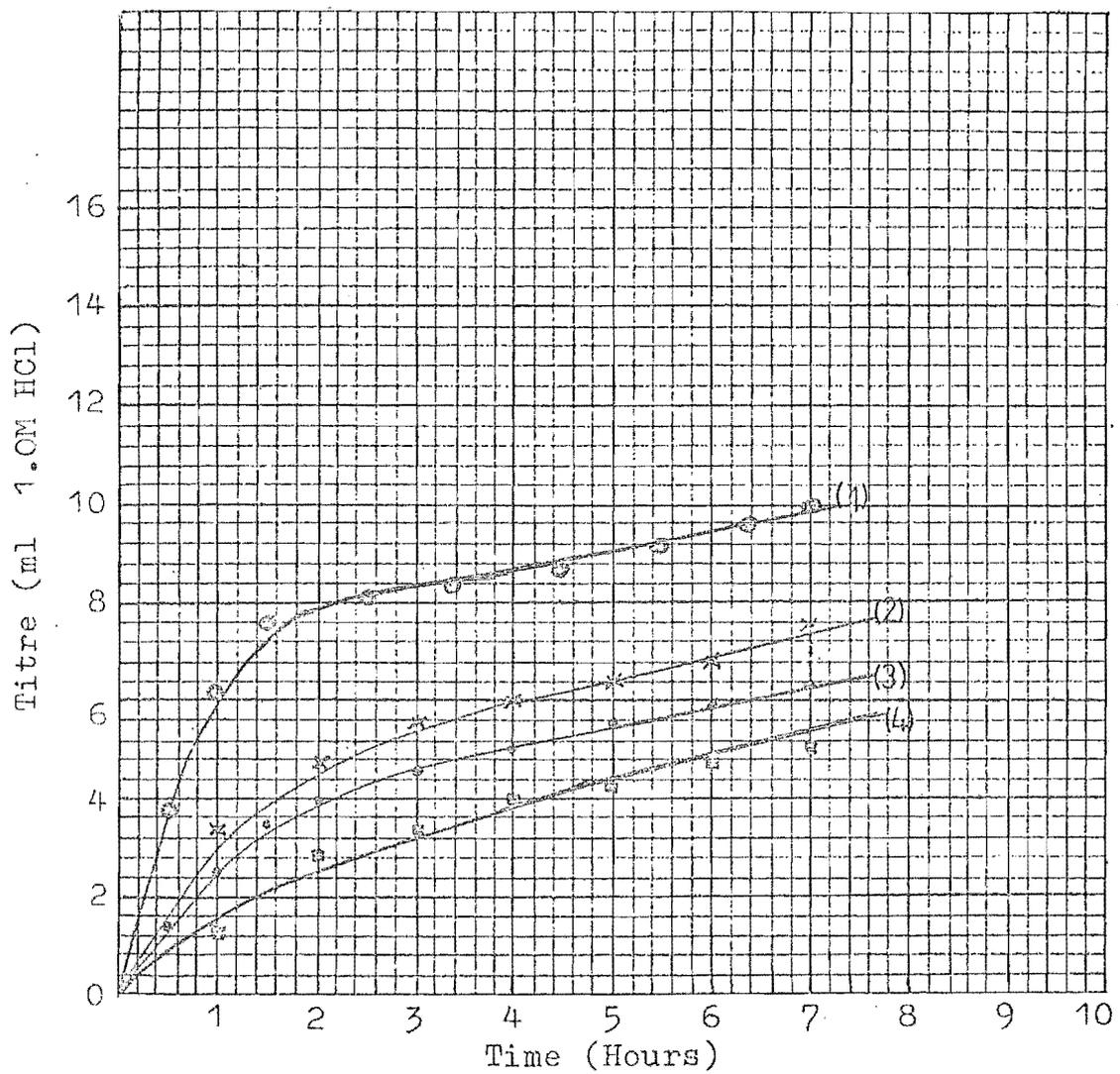
(4) Aqueous HCl/ $\text{Fe}_2(\text{SO}_4)_3$ (3 g)

pH. of leach liquor:

(1) pH = 1.8 (3) pH = 3.0

(2) pH = 1.8 (4) pH = 3.0

GRAPH 8. Effect of size change on rate of leaching.



Standard Conditions (As in graph 3)

pH of leach liquor: 2.7

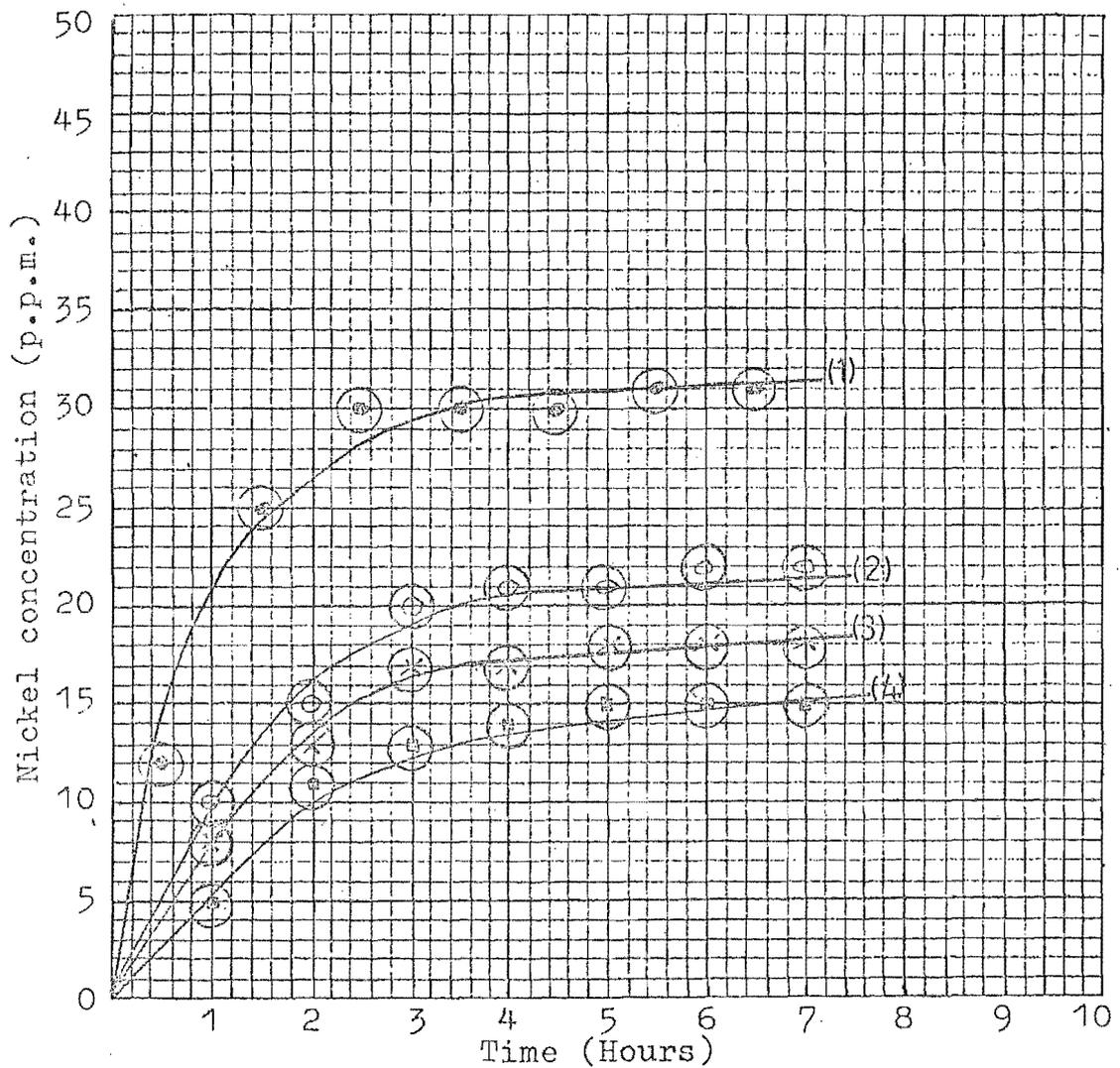
Dunite grainsize (1) Fines (Less than 177 μ)

(2) 177-250 μ

(3) 500-700 μ

(4) More than 1000 μ .

GRAPH 9. Analysis of leach liquors of graph 8.



Instrumentation: As in graph 2.

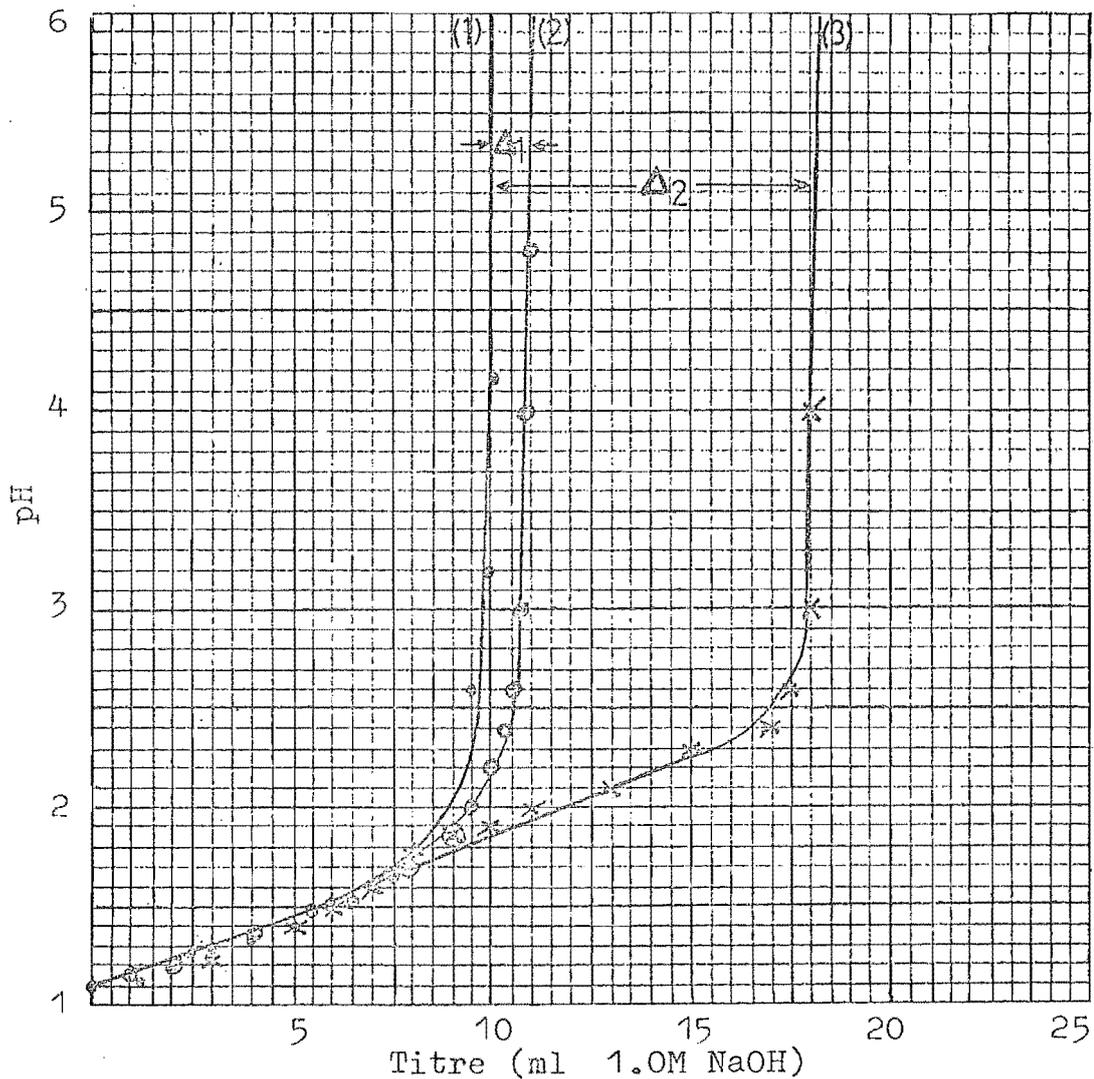
Dunite grainsize (1) Fines (Less than 177 μ)

(2) 177-250 μ .

(3) 500-700 μ .

(4) More than 1000 μ .

GRAPH 10. Determination of solubility of nickel dimethylglyoxime in dilute acids.

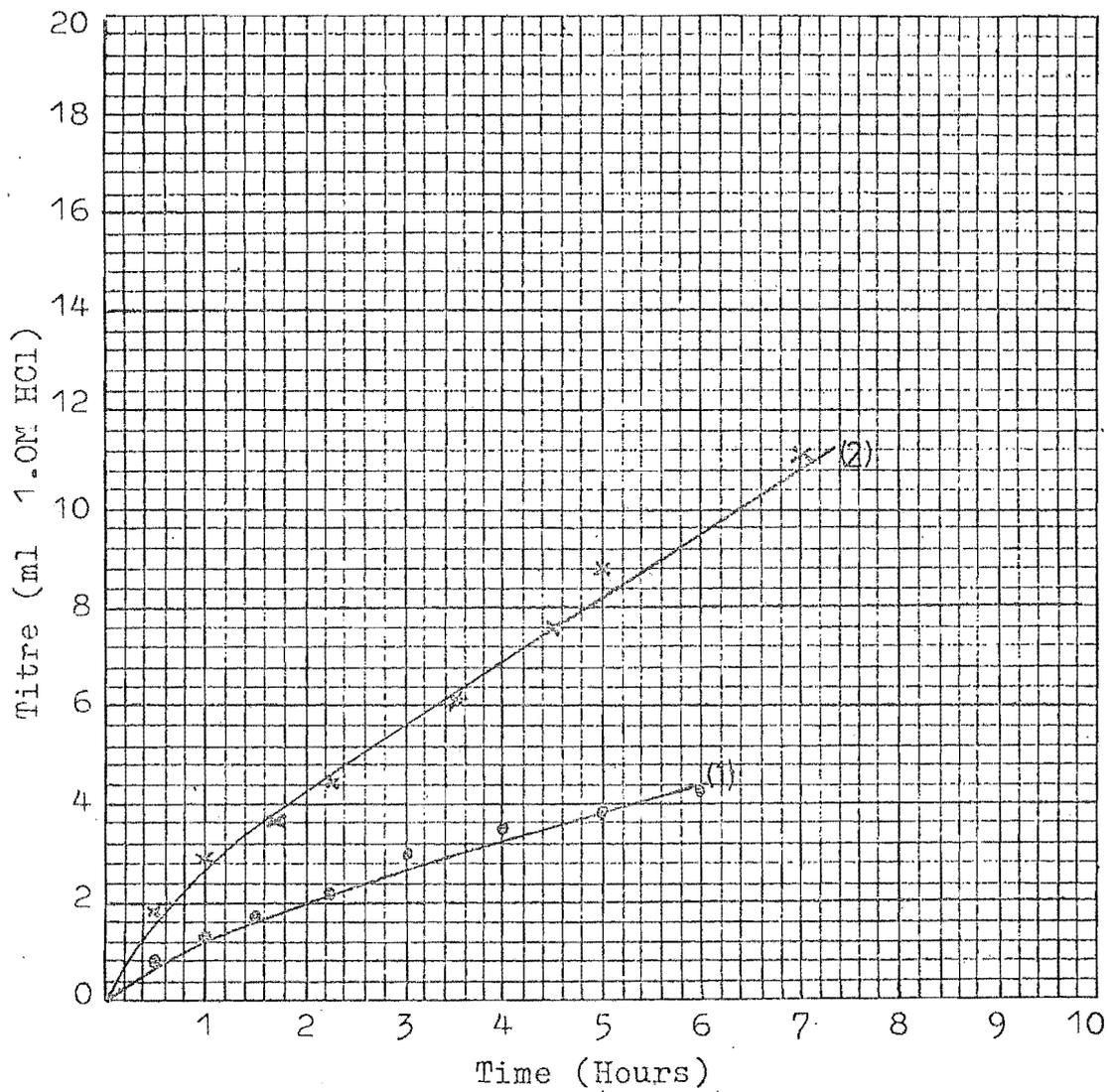


Curve (1) - Titration of 0.104 M HCl against 1.0 M NaOH

(2) - Titration of 0.104 M HCl/.105 g. NiSO₄/.10 g. dimethylglyoxime (D.M.G.) solution against 1.0 M NaOH.

(3) - Titration of 0.104 M HCl/1.05 g. NiSO₄/1.0 g. D.M.G. solution against 1.0 M NaOH.

GRAPH 11. Acid/complexing agent solutions as leaching media.



Standard conditions (As in graph 3)

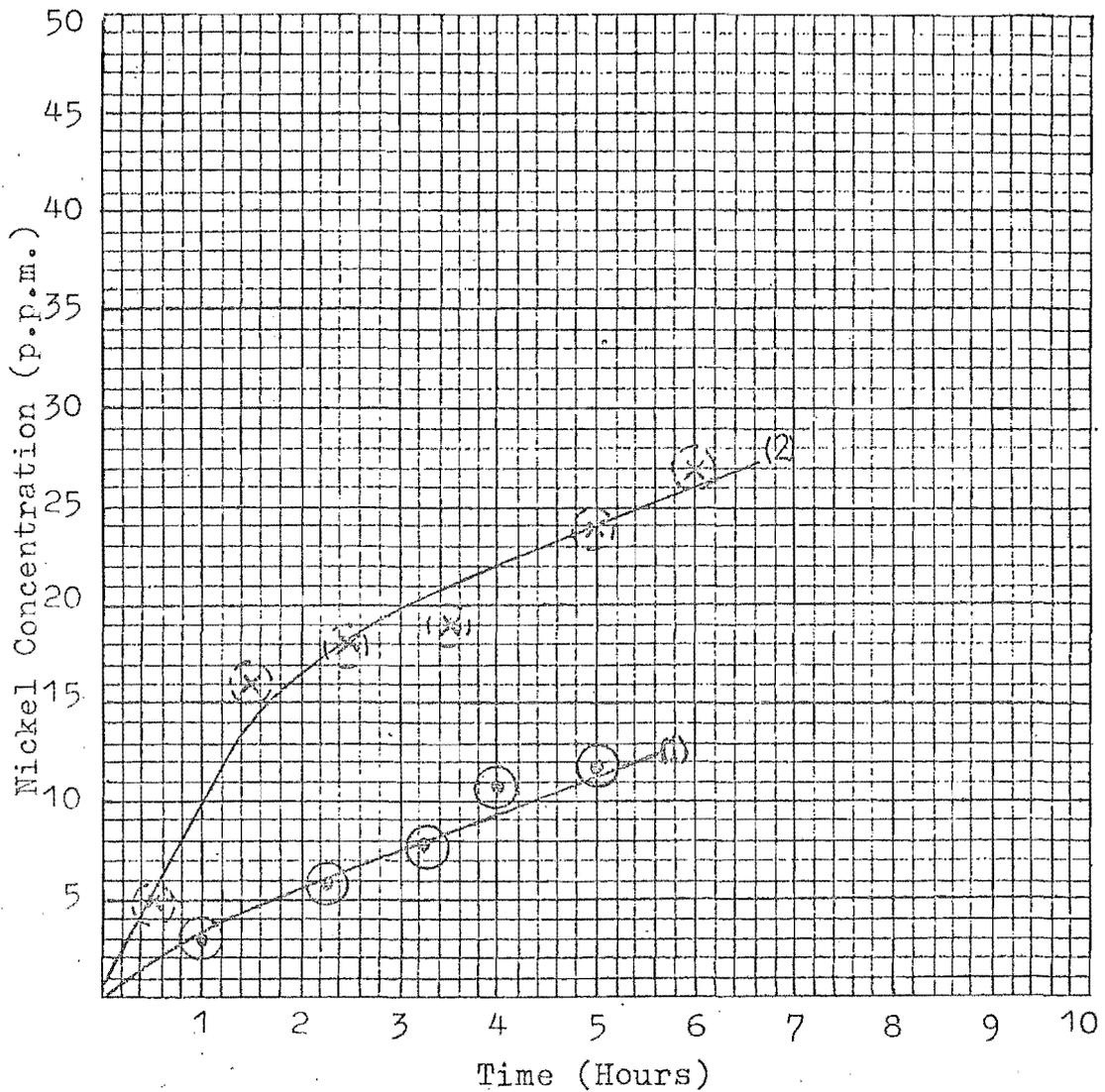
pH of leaching solution: 3.0

Composition of leach liquor: (1) Aqueous HCl

(2) Aqueous HCl/0.01M

E.D.T.A

GRAPH 12. Analysis of leach liquors of graph 11.



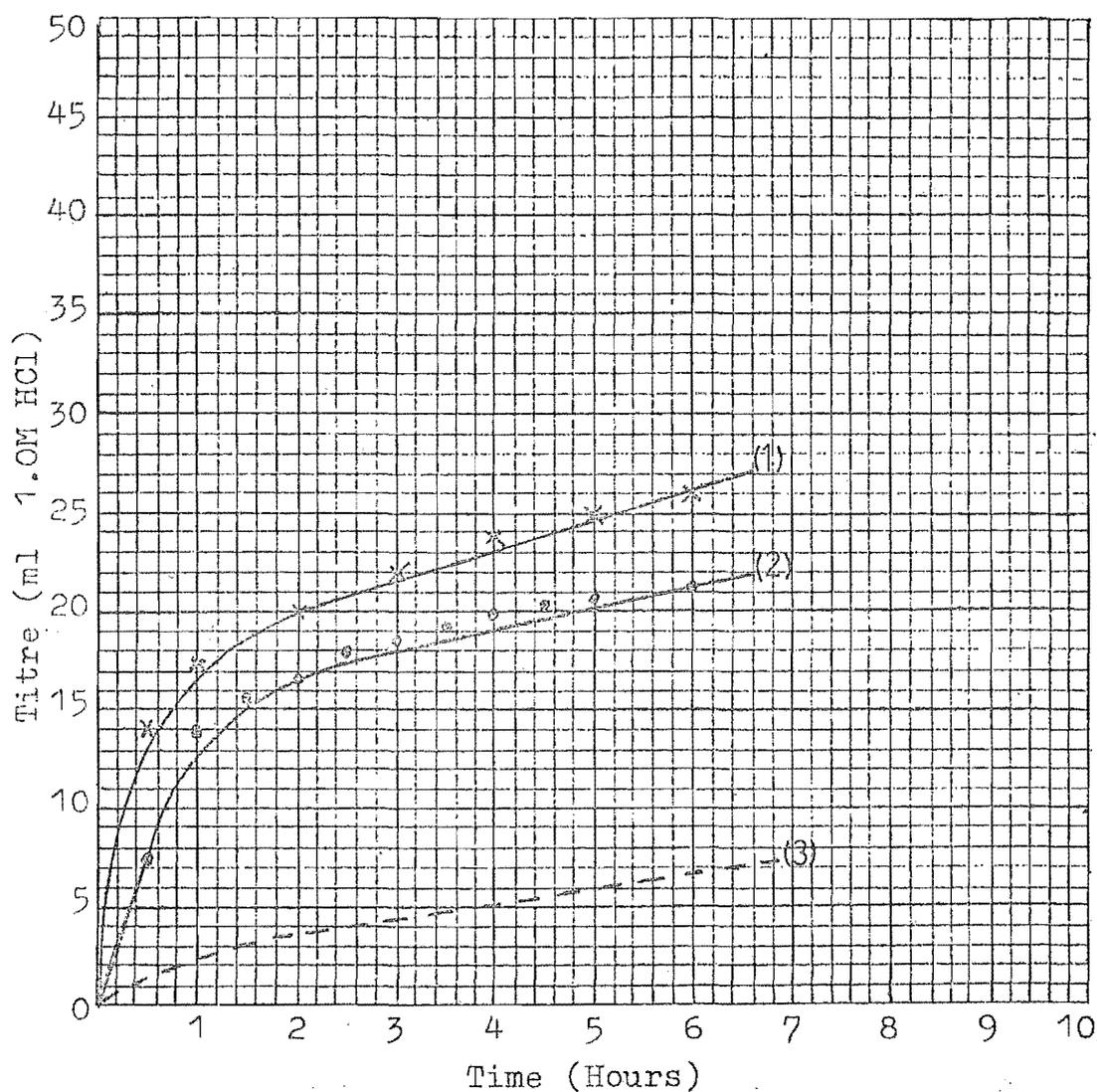
Instrumentation: As in graph 2.

Composition of leach liquor: (1) Aqueous HCl

(2) Aqueous HCl/0.01 M

E.D.T.A.

GRAPH 13. Effect of oxidative roasting on acid consumption.



Standard Conditions (As in graph 3)

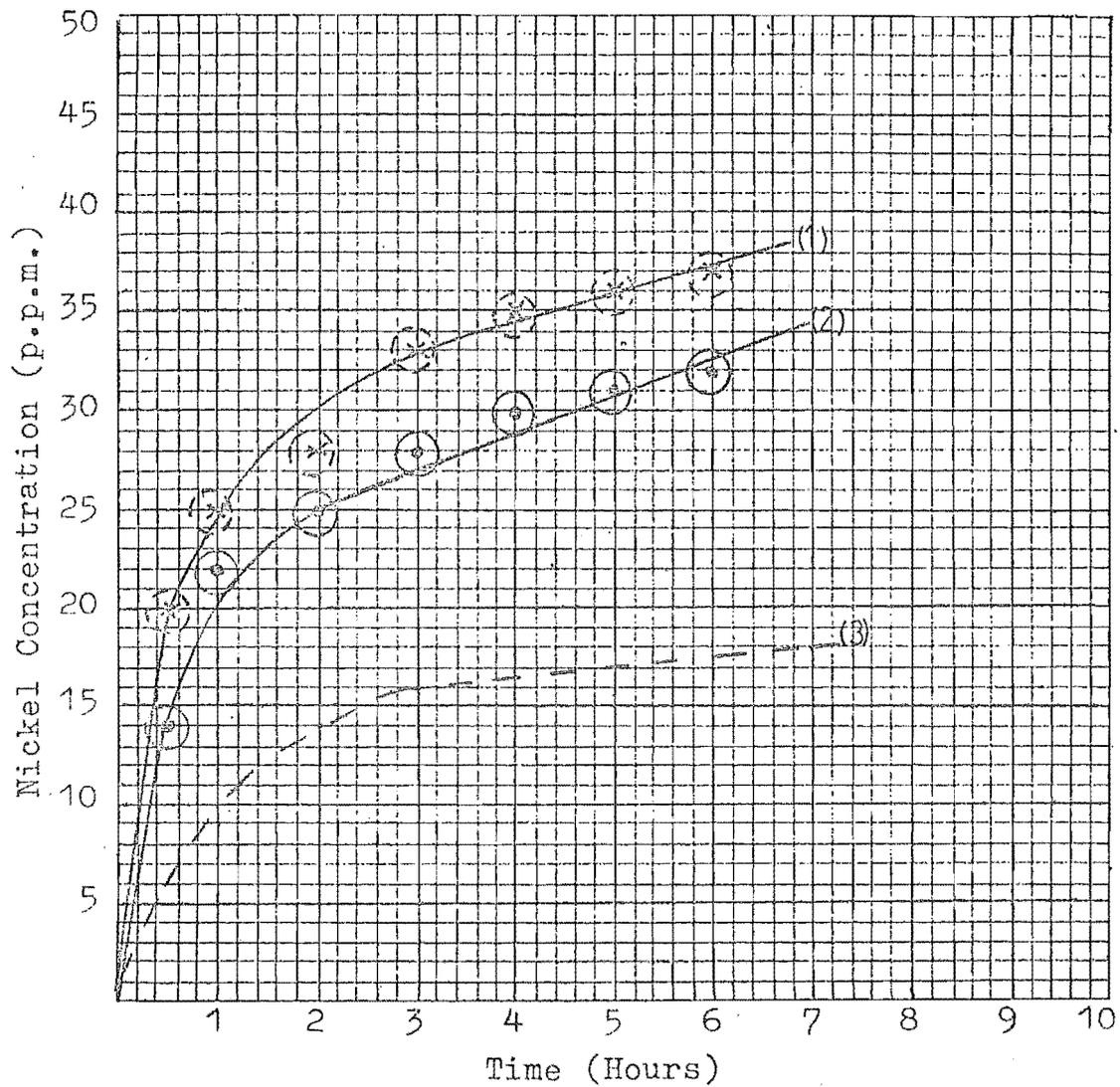
pH of leach liquor: 2.5

Curve (1) Dunite roasted at 500°C for 18 hours.

Curve (2) Dunite roasted at 500°C for 3 hours.

Curve (3) Standard untreated dunite.

GRAPH 14. Analysis of leach liquor of graph 13.



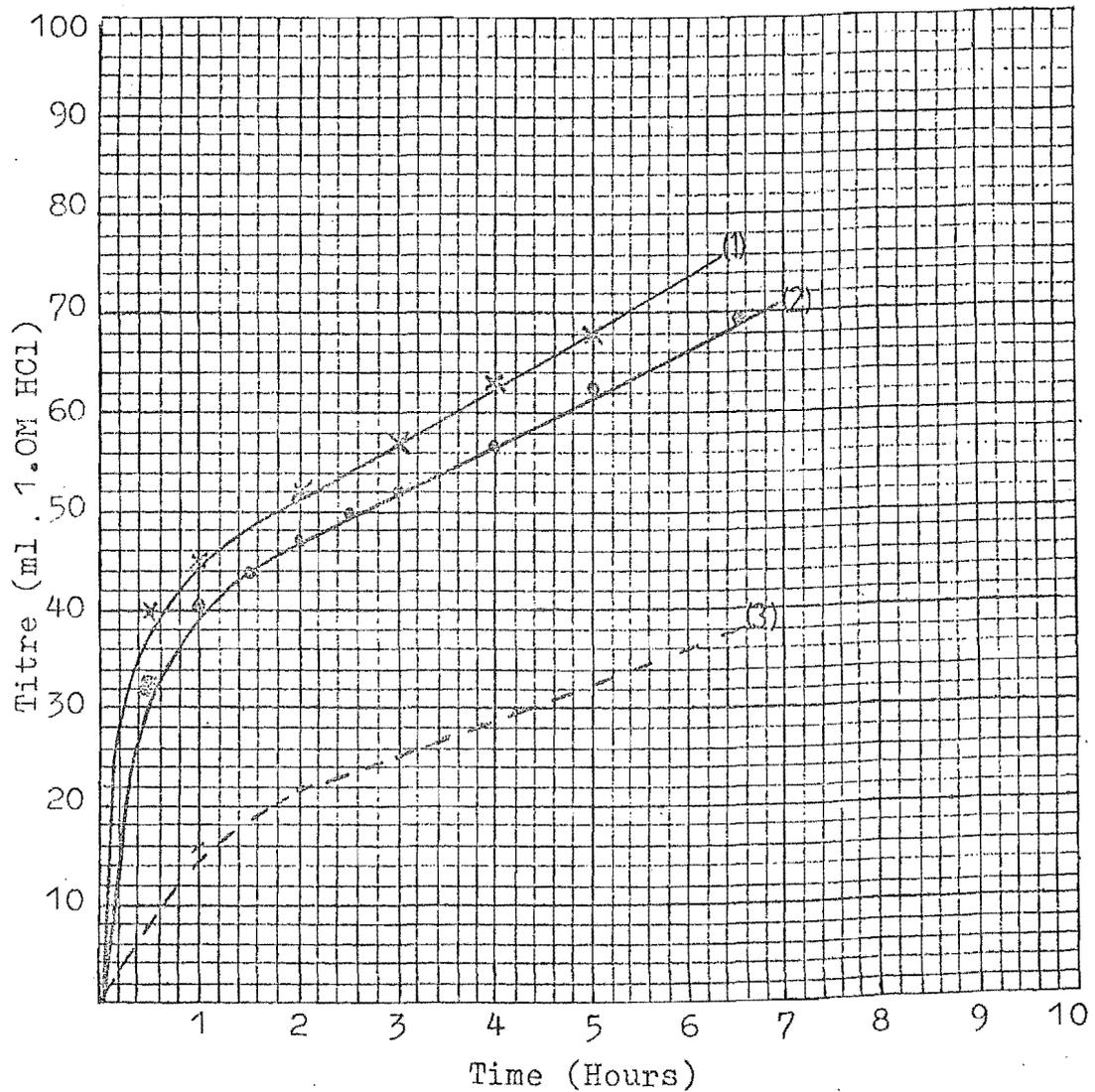
Instrumentation: As in graph 2.

Curve (1) Dunite roasted at 500°C for 18 hours.

Curve (2) Dunite roasted at 500°C for 3 hours.

Curve (3) Standard Untreated dunite.

GRAPH 15. Effect of oxidative roasting on acid consumption.



Standard Conditions (As in graph 3)

Composition of leach liquor: Aqueous HCl

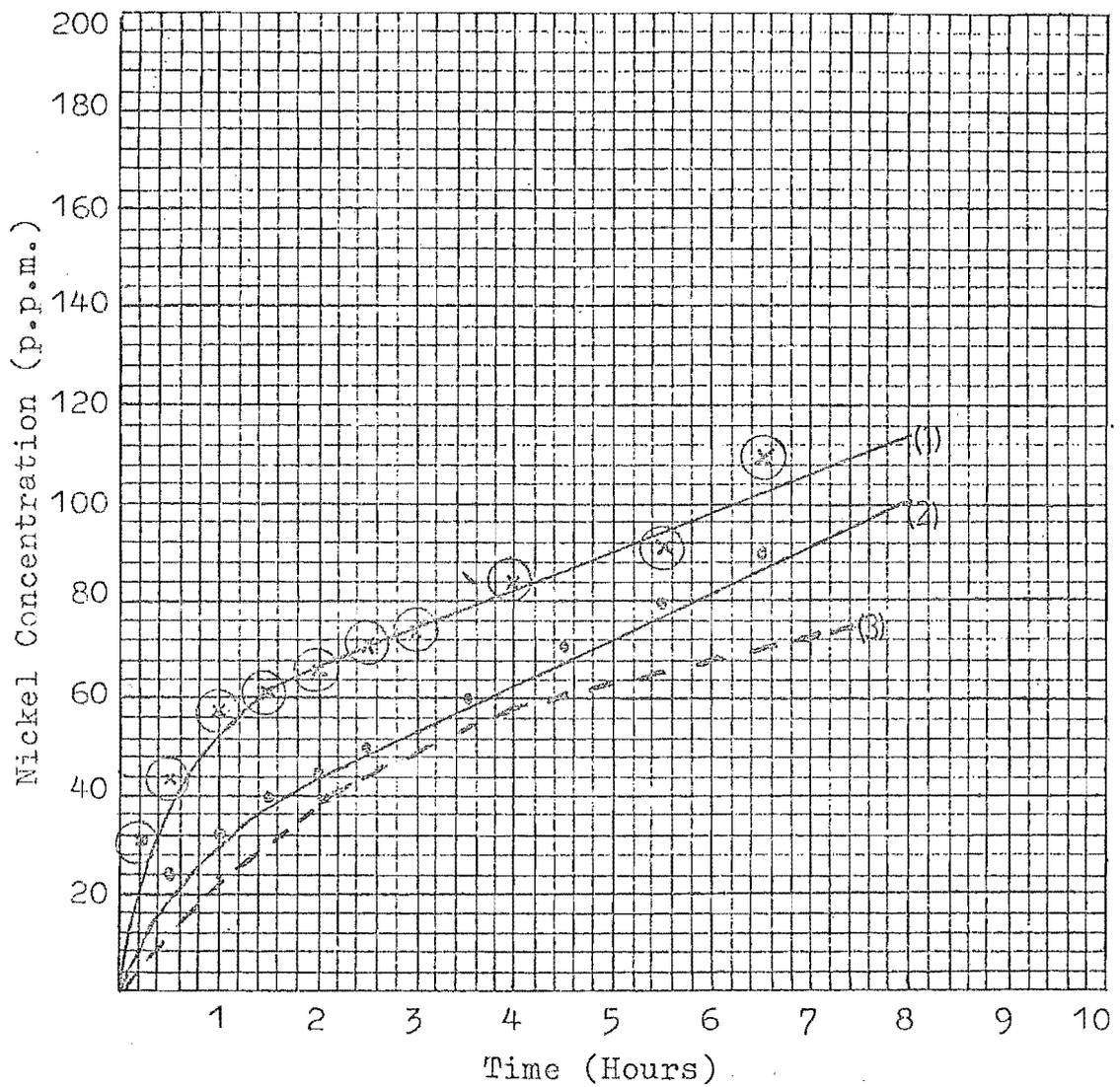
pH of leach liquor: 1.0

Curve (1) Dunite roasted at 500°C for 18 hours.

Curve (2) Dunite roasted at 500°C for 3 hours.

Curve (3) Standard untreated dunite.

GRAPH 16. Analysis of leach liquors of graph 15.



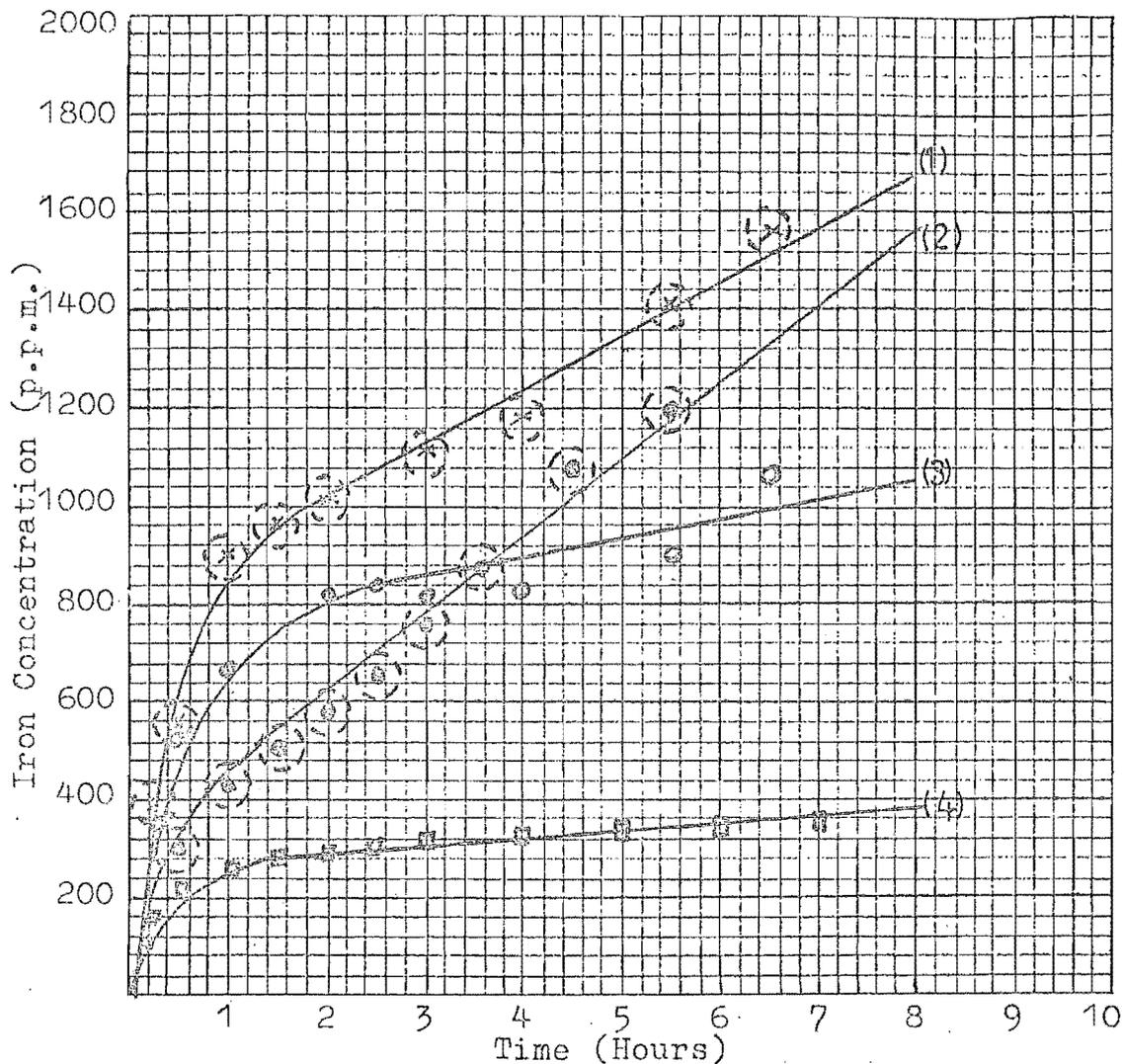
Instrumentation (As in graph 2)

Curve (1) Dunite roasted at 500°C for 18 hours.

(2) Dunite roasted at 500°C for 3 hours.

(3) Standard untreated dunite.

GRAPH 17. Total Iron/Ferric ion analysis of leach liquors of graph 15.



Total Iron Analysis (Atomic Absorption)

Curve (1) Roasted Ore (3 hours; 500 deg.C.)

Curve (2) Unroasted Ore.

Instrumentation: As in graph 2.

Monochromator Setting: 248.3 nm.

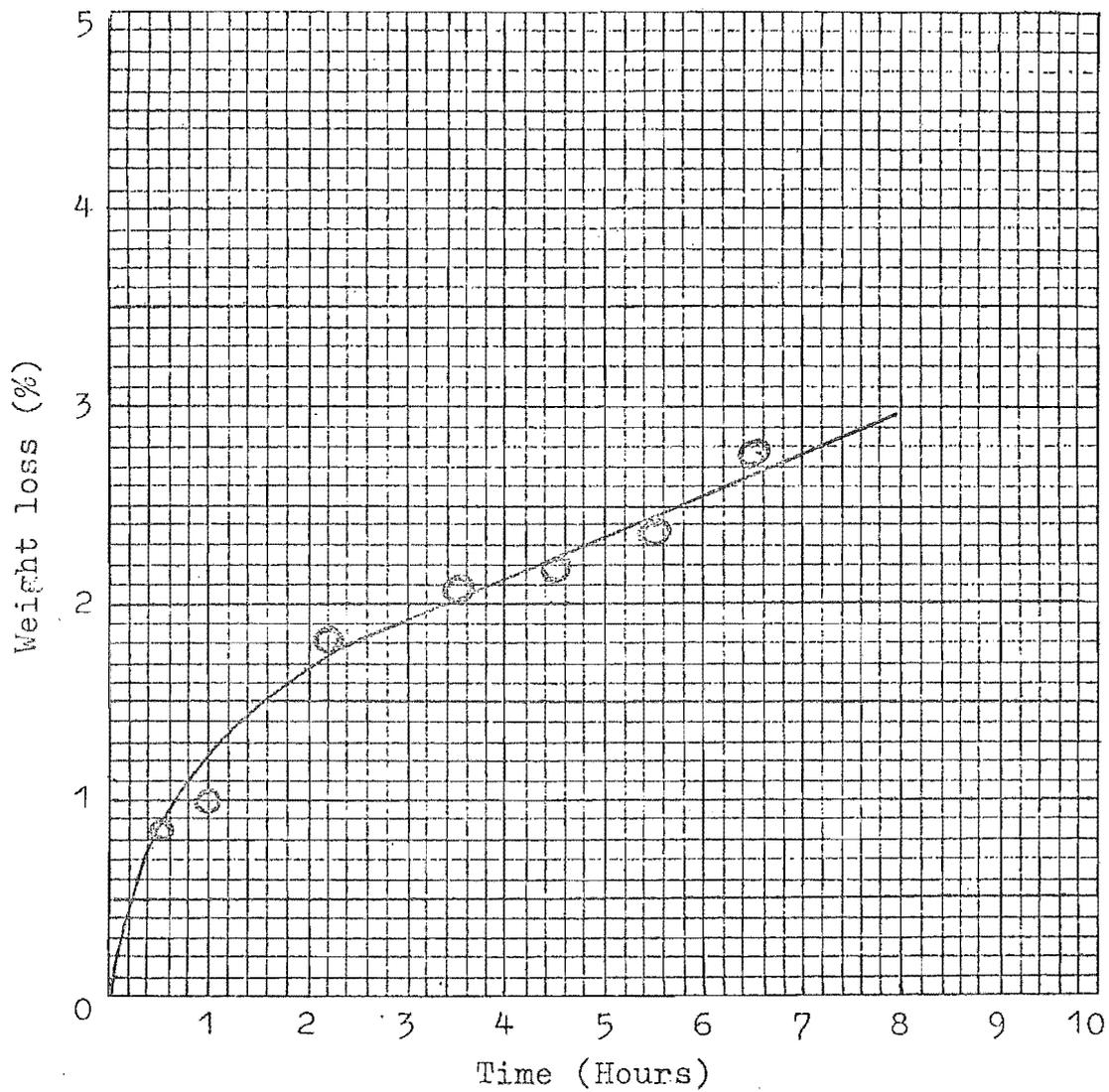
Slit Width: 100 μ .

Ferric Ion Analysis (Thiocyanate Method ⁵⁴)

Curve (3) Roasted Ore (3 hours; 500 deg.C.)

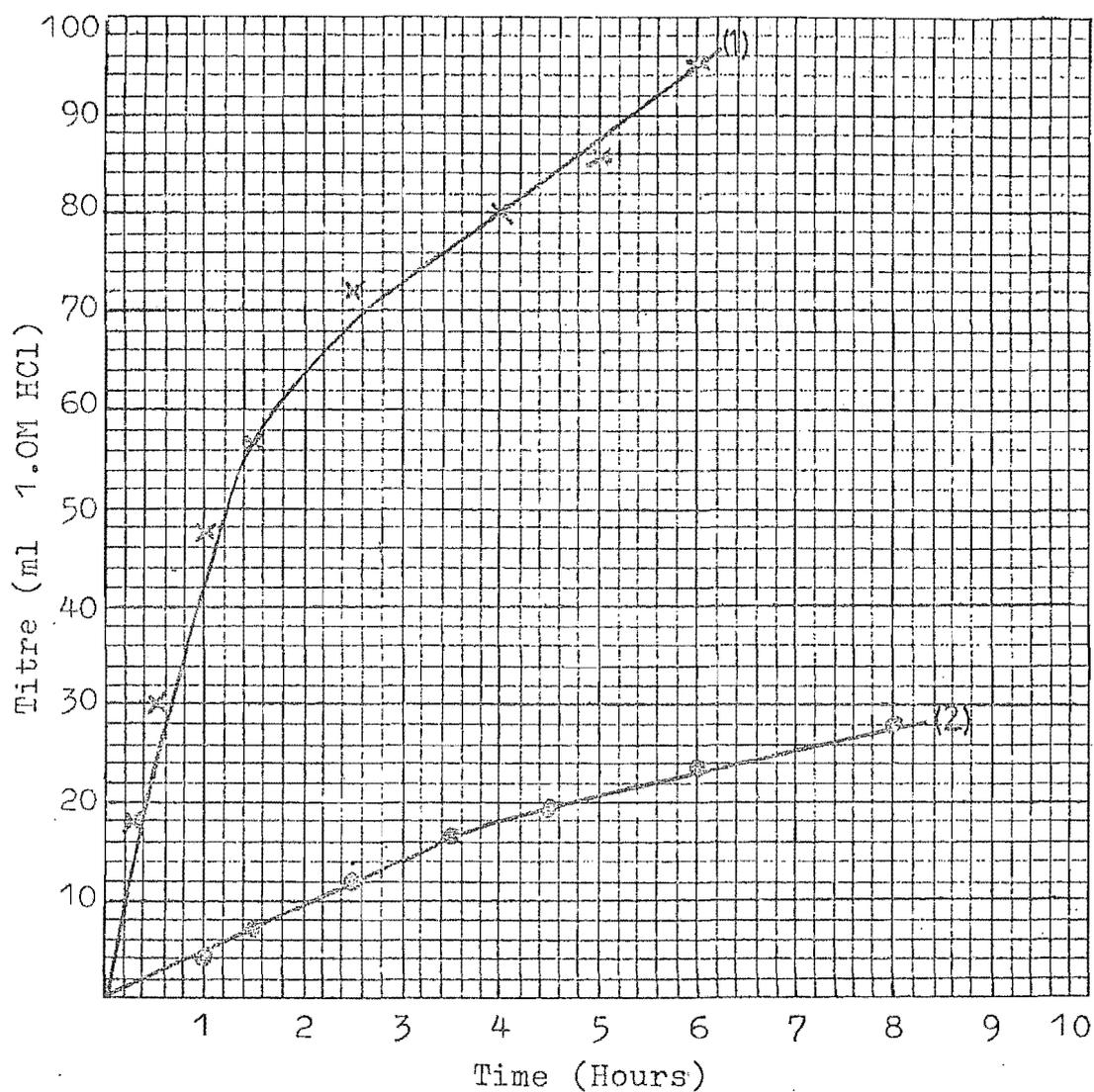
Curve (4) Unroasted Ore.

GRAPH 18. Percentage weight loss during oxidative roasting.



Temperature of roasting: 500°C.

GRAPH 19. Effect of pre-reduction on leaching rate.



Standard Conditions: As in graph 3.

Reducing agent: Coal dust.

Time of reduction: (1) $1\frac{1}{2}$ hours.

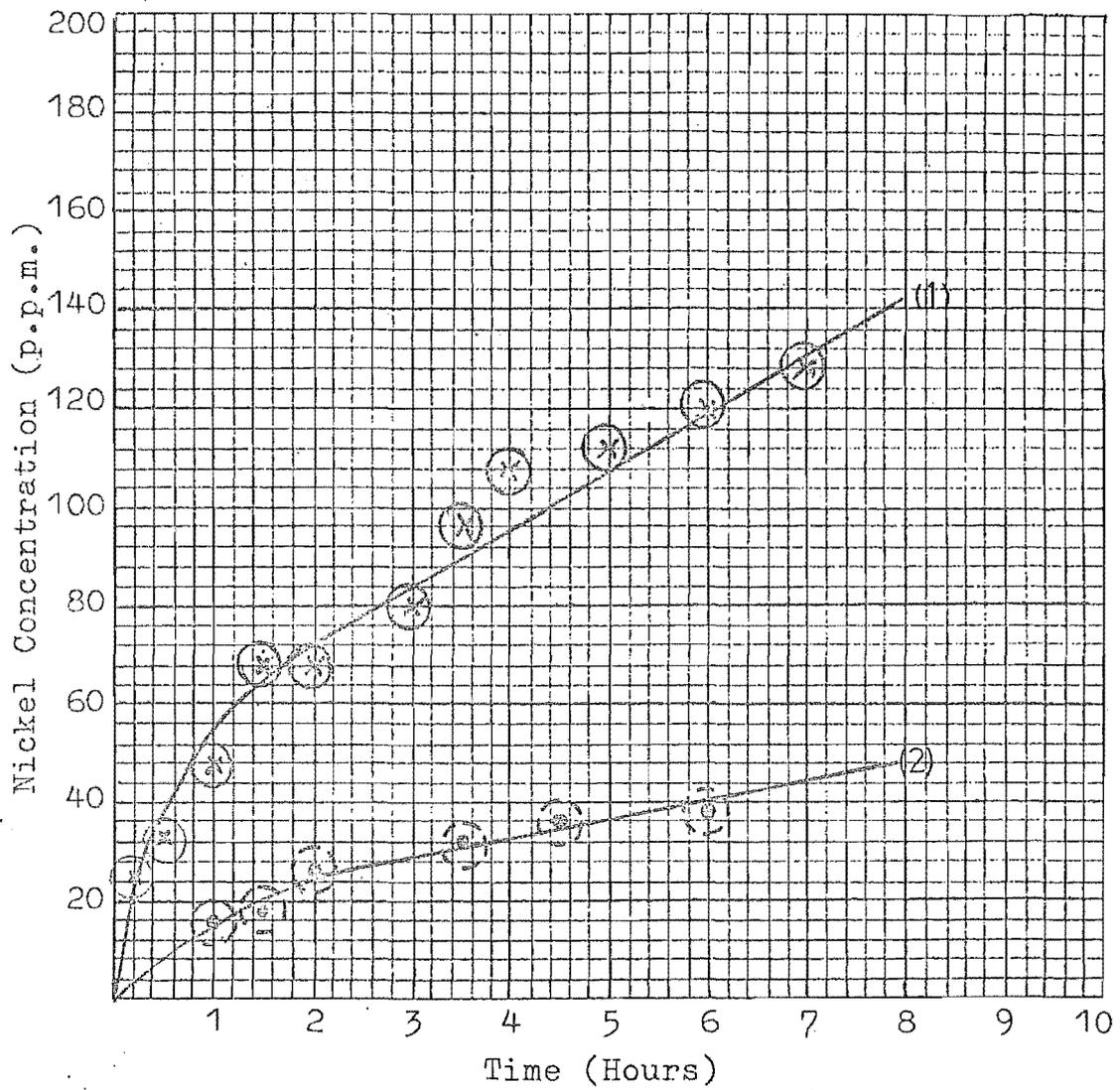
(2) 1 hour.

pH of leaching solution: (1) 1.0

(2) 2.5

Composition of leaching solution: Aqueous HCl.

GRAPH 20. Analysis of leach liquors of graph 19.

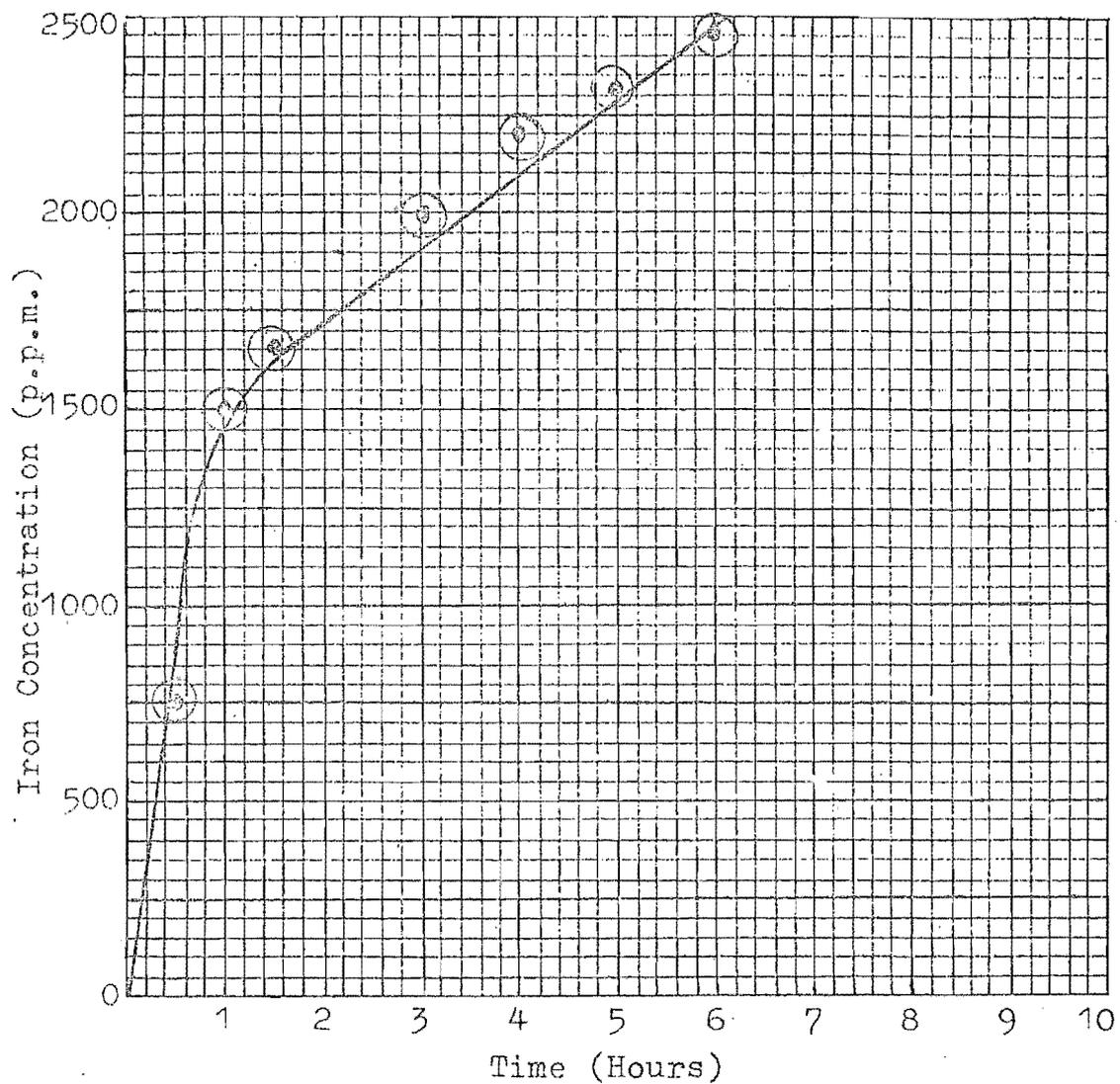


Instrumentation: As in graph 2.

Curve (1) pH = 1.0

Curve (2) pH = 2.5.

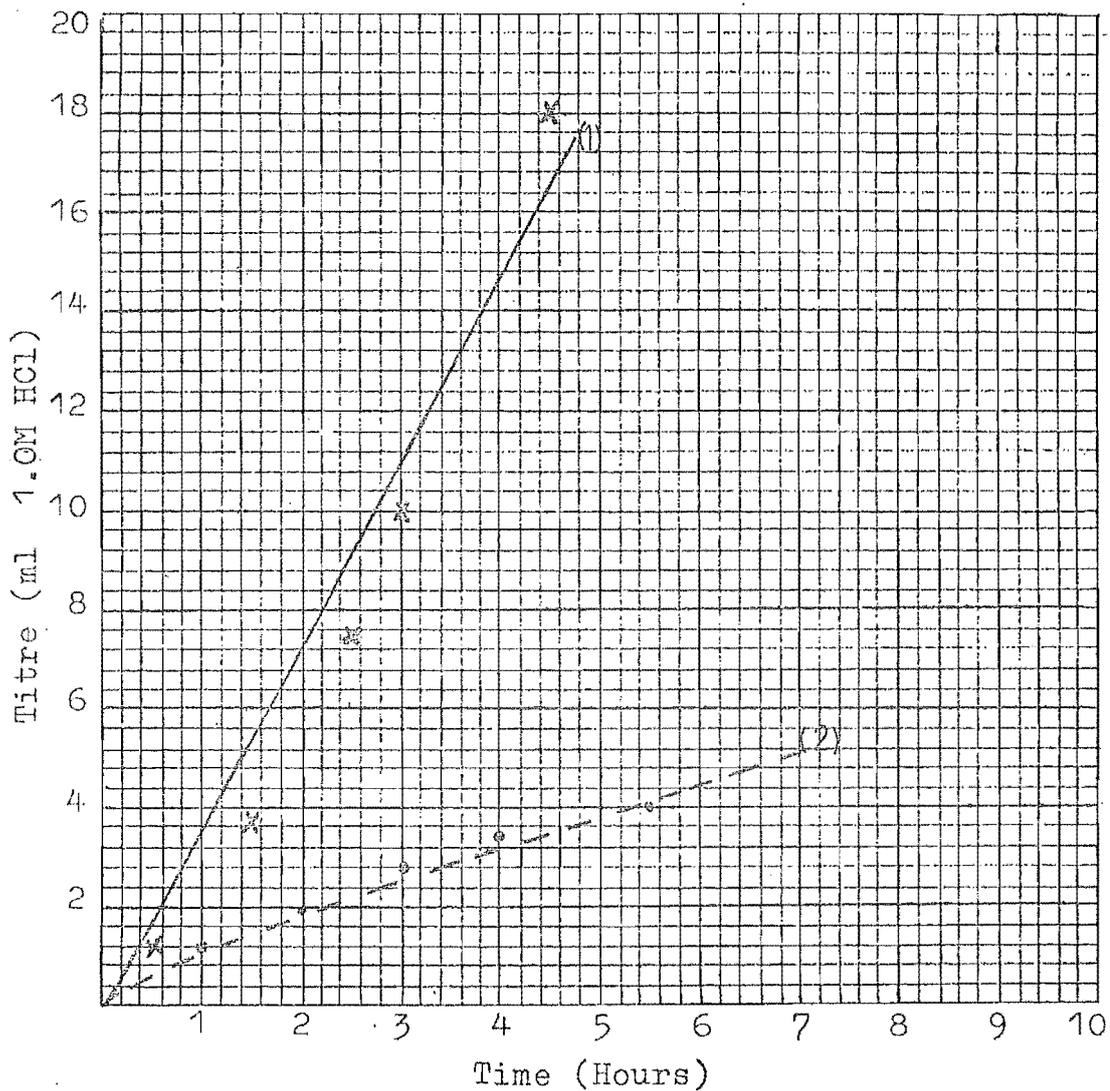
GRAPH 21. Iron analysis of leach liquors of graph 19.



Instrumentation: As in graph 17.

pH = 1.0.

GRAPH 22. Effect of chelating agent upon leaching
of pre-reduced ore.



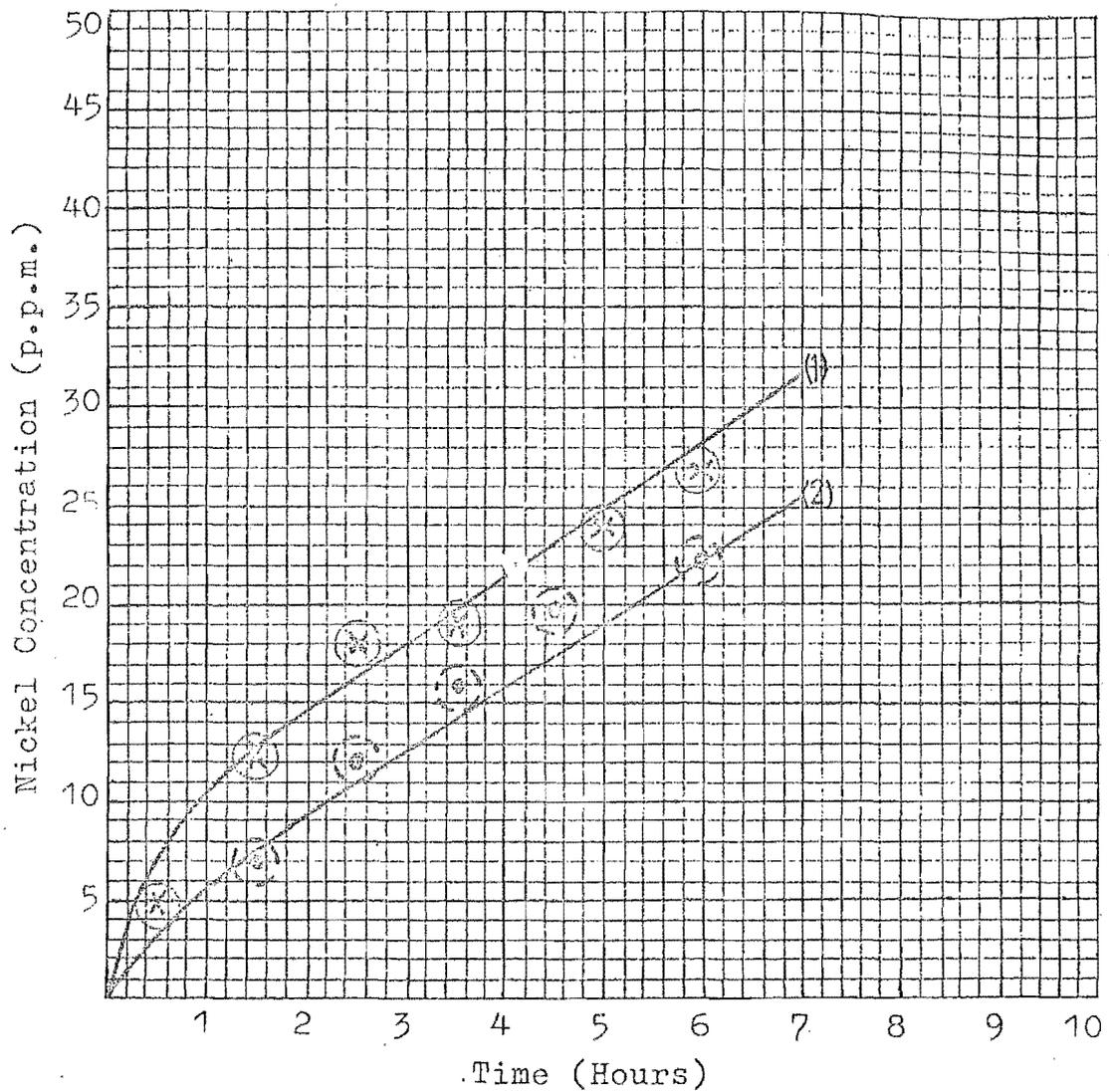
Standard Conditions: (As in graph 3)

pH of leach liquor: 3.0

Composition of leach liquor (1) Aqueous HCl/0.1M E.D.T.A.

(2) Aqueous HCl.

GRAPH 23. Analysis of leach liquors of graph 22.



Instrumentation: As in graph 3.

Composition of leach liquor (1) Aqueous HCl/0.1M E.D.T.A.

(2) Aqueous HCl

CHAPTER THREE

DISCUSSION OF RESULTS

3.1. RESULTS OF LEACHING STUDIES ON UNTREATED ORES.

(a) Acid Leaching. Sanemasa, Yoshida and Ozawa⁴⁶ studied the dissolution of olivine in aqueous solutions of inorganic acids at 35, 50 and 65°C. The olivine was derived from a crushed dunite sample by magnetic separation and was sized by sedimentation to a 10-20 μ range. Leaching was effected by slurring in .005-2.0 N perchloric, sulphuric, and hydrochloric acids. They observed that the slope of the leaching curve (change in leached metal ion concentration with time) was not constant throughout the reaction. The leaching curve was composed of two straight lines - an initial line (up to approximately 5% dissolution) and a "secondary" line of lesser slope. They further observed that the rate of dissolution was first order with respect to the surface area of the ore particles and that the olivine was leached by inorganic acid solutions without any selective dissolution of the components of the mineral. Sulphuric acid and solutions of bisulphate ion in HCl (aq) or HClO₄ (aq) were observed to react much more quickly than hydrochloric or perchloric acid solutions of comparable normality.

A similar study reported in this thesis (graphs 1 and 2) confirmed these observations with the exception

of the bisulphate ion effect. Comparable strengths of hydrochloric and sulphuric acids (graph 1) were seen to react at similar initial rates and to yield similar concentrations of nickel ion (graph 2). The major differences in experimental conditions under which these observations were made were:-

(i) sample size: in this work a coarse, ungraded, (0-1000 μ) sample of crushed ore was used.

(ii) pH: in this work the pH was maintained constant during the leaching process; in contrast Sanemasa reacted the ore with comparatively concentrated acids which were consumed (pH increasing) during the reaction. The marked difference in reactivity between hydrochloric and sulphuric acids reported by Sanemasa is of interest. It has been suggested⁵⁵ that the enhanced rate of bisulphate ion attack may be due to dipole interactions between the HSO_4^- ion or $\text{H}^+ \text{---} \text{SO}_4^{2-}$ ion pairs and active sites on the solid surface. It is possible that in Sanemasa's studies the observed effect arises from the buffering action of HSO_4^- as the pH varies throughout the region 1.5 - 2.5. When, as in this work, the leaching is effected at constant pH there is no specific reactivity associated with sulphuric acid.

Urazov and Bogatsky³⁴ investigated the effects of hydrochloric, sulphuric and nitric acids on a garnierite/cerolite/deweylite ore and concluded that, for nickel leaching, nitric acid was less efficient than hydrochloric acid which in turn was inferior to sulphuric acid. However, this ore differs significantly from olivine in both

chemical and physical properties.

The "two slope" nature of the leaching curve reported above is again evident upon consideration of the effect of changing pH on the extraction rate (graph 3). The initial slope persists for a similar period in each experiment with the greater slope corresponding to the lower pH. The secondary portion of the curve changes similarly with pH; continuation of the reaction for a protracted period (15 hours) causes no further reduction in reaction rate. The form of the nickel release curve (graph 4) is similar to that of the acid consumption curve, the nickel concentration rising rapidly initially then less rapidly as the reaction proceeds.

It was observed that the yield of nickel per mole of acid consumed varied both with time and pH. As illustrated in the curve below:-

(i) at constant pH the ratio $\text{Ni}^{2+}/\text{H}^{+}$ decreased with time.

(ii) the ratio $\text{Ni}^{2+}/\text{H}^{+}$ was higher at high pH i.e. the reaction produces a lower yield of nickel at high acidity.

This concept of "leaching efficiency" implies a degree of selectivity in the removal of nickel ions at a higher pH. For a typical curve (e.g. graph 5; curve 4), the percentage of entrained nickel leached from the ore after the initial period ($1\frac{1}{2}$ hours) was about 2% while after 8 hours about 3% of the nickel was leached.

(b) Acid/Excess Metal Ion Solutions as Leaching Agents. After the period of rapid initial reaction the concentration of metal ions in the leach solution is observed to increase at an essentially constant rate. As the reaction proceeds the leach liquor would thus be considerably enriched in dissolved cations. It was not practicable to follow the leaching process to completion yet it was of interest to ascertain the effect on the leaching process of the increasing concentrations of magnesium and iron during the latter stages of the reaction. This was examined by adding a solution of the leached ions at an early stage of the reaction. The ions were added as small aliquots of solution at the same pH as the leachate and in such concentrations as to be equivalent to 25% of the total metal content of the dunite present. When ferrous ion was added after seven hours the acid titre increased suddenly (graph 5; curve 3). Addition of ferrous ion prior to reaction (graph 5; curve 1) gave a similar overall increase in the acid consumption.

Magnesium ion (graph 5; curve 2) added prior to the reaction gave the same increase in acid titre even though the molar concentration of magnesium was four times greater than that of ferrous iron. Nickel ions in very low concentrations (corresponding to the small amount of nickel present in olivine) gave no appreciable increase in acid uptake but addition of a small amount of saturated nickel sulphate solution reproduced the effect satisfactorily.

Addition of increased quantities of iron or of repeated aliquots of solution gave no further increase in acid consumption. In each case the increase in acid uptake was paralleled by a proportionate increase in the concentration of released nickel (graph 6). The observed metal ion effect is specific to divalent metal ions. The addition of the smaller and more highly charged aluminium ion produced no effect.

Any attempt to rationalize this effect must explain several observations:-

(i) the effect is specific to divalent cations,

(ii) the effect cannot be enhanced or reproduced by addition of increased concentrations or of successive aliquots of metal ion,

(iii) the effect is accompanied by an increased release of nickel proportional to the amount of acid consumed;

(iv) the slope of the secondary portion of the curve is unchanged; i.e. the effect is almost instantaneous

and the rate of acid leaching of the dunite is similar before and after excess metal ion addition.

These observations indicate a co-operative metal/proton reaction. Clearly the rate of initial (surface?) reaction is enhanced by the presence of metal ions. Similarly the reaction rate, at any point in time, may be accelerated by addition of such ions.

The formation of an insoluble basic magnesium silicate mineral clino-chrysotile ($\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$) in the reaction suspension may be of significance in the interpretation of these observations. The mineral, which appeared as a white suspension in the reacting solution, was initially thought to be fine dunite material formed in the highly abrasive stirred slurry. Comparison of this material (obtained by filtration from the supernatant reaction suspension) with powdered dunite by x-ray powder diffraction indicated significant differences in structure. New x-ray reflections were evident (superimposed on a background of dunite reflections) corresponding to d values of 7.37, 3.63, and 1.54 Å (refer page 63). Clino chrysotile ($\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$) has powder lines with d spacings of 7.36, 3.66, 2.45, and 1.53 Å with relative intensities of 100, 80, 65, 65. The corresponding nickel analogue $(\text{Ni},\text{Mg})_3\text{Si}_2\text{O}_5(\text{OH})_4$ produces similar d spacings.

Exactly when the mineral is formed in solution is not clear. The characteristic powder photograph is obtained after several hours of reaction and even at this time is superimposed only faintly upon a

characteristic dunite background. If the reaction proceeds via a nickel, magnesium intermediate similar to this basic silicate then addition of ferrous or magnesium ion could enhance nickel release. Clinochrysotile consists of kaolin-like layers which are not planar but stacked in a helical manner.⁵⁶ The vulnerability of nickel ions in this open structure suggests that they may be replaced more easily (by similar sized ions such as magnesium) than in the more massive olivine lattice. Thus the question arises as to whether the rate determining step for release of nickel is not proton substitution for nickel ions in the olivine lattice but rather cation substitution for nickel in the chrysotile lattice.

Ferric ion has been suggested by several authors (among them Bogatsky and Urazov³⁴ Kryukova³⁸ and Greene²⁷) as a leachant for nickel ores. However, the observed effect of ferric ion solutions on dunite leaching (graph 7) was to retard the uptake of acid. Addition of ferric ion during the reaction (graph 7, curve 2) caused a decrease in the rate of uptake of acid, the rate dropping to zero for a time. Addition of ferric ion prior to the reaction (curve 4) resulted in overall depression of the acid titre.

Ferric ion is strongly hydrolysed to give a solution with a pH of about 1.5 - 2.0.



It is possible that the reported effect of ferric ion leachants relates to the formation of a buffered acid solution

(c) The Effect of Particle Size on Reaction Rate

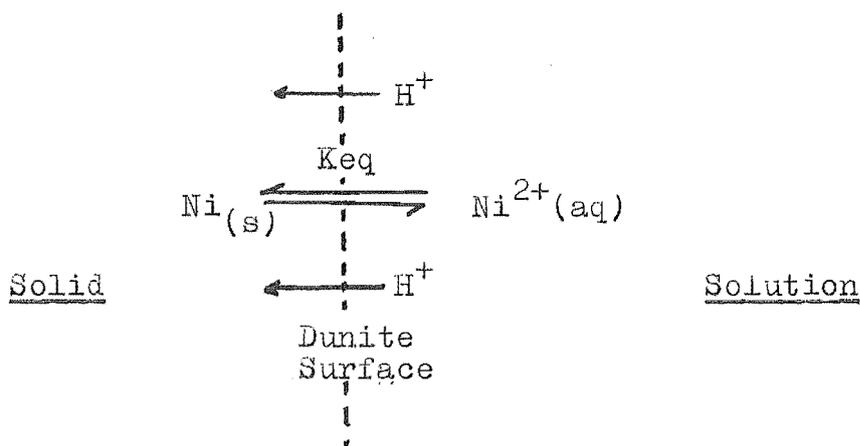
Sanemasa, Yoshida, and Ozawa observed that the rate of dissolution of olivine was first order with respect to the inverse of particle diameter. This result was reproduced in this work for a variety of grainsizes. The initial rate of reaction (i.e. the initial slope of the titre/time curve) (graphs 8 and 9) is seen to increase linearly with decreasing grainsize.

In the initial stage of the reaction (ca initial $1\frac{1}{2}$ -2 hours) the amount of acid consumed, and the amount of nickel released, is proportional to the surface area to volume ratio of the particles (i.e. inversely proportional to the size of the particles). The secondary portions of the leaching curves were however near parallel. These results may imply that the initial reaction involves the surface of the particles and that the secondary reaction is a "lattice" reaction which is independent of particle size i.e. of surface area/volume ratio.

(d) Solutions of Complexing Agents as Leachants.

The effect of an added complexing agent was considered as a possible method of improving the yield of nickel without increasing iron or magnesium release.

A solid state "lattice" reaction could involve an equilibrium at the dunite surface between the solid phase and dissolved metal ions.



If such an equilibrium exists then any change in the aqueous concentration of the metal ion would be expected to induce a change in its rate of leaching from the solid.

(i) Effect of added dimethylglyoxime. This work examined the effect of precipitation of the nickel as the sparingly soluble nickel dimethylglyoxime complex. The complex is soluble in concentrated acid solutions but becomes increasingly insoluble as the pH rises. The optimum pH for quantitative precipitation is 7.5 - 8.1.⁵⁷ In the reaction of dimethylglyoxime with nickel there is a release of protons:-

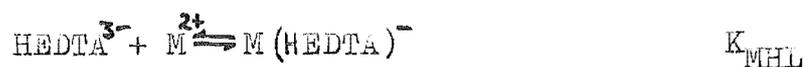


The extent of this deprotonation with increasing pH was illustrated by titrating a sodium hydroxide solution against:-

(a) standard hydrochloric acid, and
 (b) a similar acid solution containing nickel ions and dissolved dimethylglyoxime (graph 10).
 Precipitation of the nickel complex was essentially complete at pH greater than 2.5 and 50% complete at pH = 2.2.

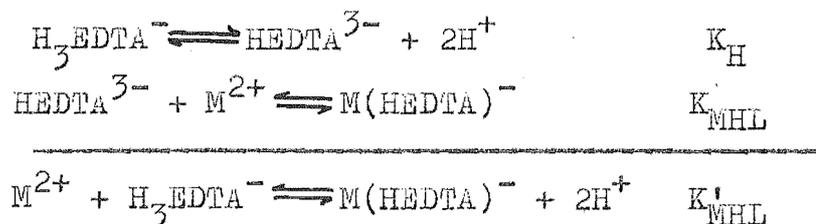
It was not possible to determine the amount of nickel leached in the presence of dimethylglyoxime as a function of time because of the inhomogeneous nature of the leaching solution (containing Ni^{2+} (aqueous) and nickel dimethylglyoxime complex). Therefore a series of bulk analysis experiments was attempted in which the total solution volume was acidified to redissolve the complex and then quickly filtered to remove the dunite grains. Results indicated no increase in nickel release in the presence of dimethylglyoxime.

(ii) Effect of added ethylenediaminetetraacetic acid (E.D.T.A.). The higher affinity of E.D.T.A. for Ni^{2+} over Fe^{2+} suggested the use of E.D.T.A. as a complexing agent to displace the possible solid/solution "equilibrium" discussed above. In a solution of pH 2-3, ethylenediaminetetraacetic acid will be present predominantly as H_3EDTA^- . Under these conditions nickel (II) and iron (II) give protonated complexes:-



with $\log K_{\text{MHL}} = 11.56$ and 6.86 for nickel and iron respectively.

Therefore at pHs between 2 and 3 the relevant equilibria will be:



where $\log K'_{\text{MHL}} = \log K_{\text{H}} (-8.83) + \log K_{\text{MHL}}$

This gives:

$$\log K'_{\text{NiHL}} = 2.8 \text{ and } \log K'_{\text{FeHL}} = -1.9$$

At any pH the ratio $K'_{\text{NiHL}}/K'_{\text{FeHL}} = K_{\text{NiHL}}/K_{\text{FeHL}}$

$$= 10^{4.7}$$

i.e. Nickel will be preferentially complexed in the presence of iron.

Choosing $[\text{H}_3\text{EDTA}^-] = 0.01\text{M}$ and assuming Ni^{2+} much less than H_3EDTA^-

$$\text{Then } - \frac{[\text{NiHEDTA}^-]}{[\text{Ni}^{2+}]} = \frac{0.01 \times 10^{2.8}}{[\text{H}^+]^2}$$

$$= 10^{6.8} \text{ at pH } = 3$$

$$\text{or } = 10^{4.8} \text{ at pH } = 2 \text{ (cf. } 10^{0.1} \text{ for iron)}$$

i.e. Most of the nickel will be complexed.

The experiments were performed at pH=3.0 and EDTA = 0.01M. In the presence of EDTA the rate of nickel release (graph 12) was observed to increase but the acid titre (graph 11) increased by a similar factor.

An apparent enhancement during the initial phase does not carry over into the secondary phase of the reaction. This supports the concept of a surface abrasion effect as the rate determining factor. Such a result is in keeping with the observations of Mase⁴⁰ who undertook a similar study of the leaching of olivine by boiling E.D.T.A. solution.

3.2 RESULTS OF LEACHING OF PRETREATED ORES.

(a) Oxidative Roasting. Mase³⁹ reported that the solubility of olivine in acids could be increased by calcination at temperatures in excess of 500°C. In an experiment (graphs 13 and 15) the dunite grains were heated, with free access of air, in a muffle furnace at temperatures of about 550°C for various periods of time. The consumption of acid by this treated dunite (under similar reaction conditions to those described earlier) increased markedly. The nickel release, although also increasing significantly, did not increase by the same factor (graphs 14 and 16).

Graph 17 illustrates an analysis of the leach liquor for divalent and trivalent iron. The ferrous/ferric ion ratio in untreated dunite rock is about 10:1. As may be expected the proportion of total iron present in the ferric state increased significantly with roasting. Substitution of each ferric ion by acid requires one extra proton and consequently oxidation of iron increases

its acid uptake by 50%. Most of the iron (III) is released in the initial $\frac{1}{2}$ - $\frac{3}{4}$ hour of reaction suggesting that in this period a surface reaction is involved and that oxidation of the iron occurs only on the surface of the ore. The iron (II) release (difference between total iron and iron (III) concentrations) is approximately independent of ore treatment, suggesting that it results from a lattice reaction.

The analysis of nickel solutions containing large concentrations of ferric ion (such as the above leach liquor) is not without problems. Interference is found to be significant in some cases of atomic absorption spectroscopy^{58,59} and in a comprehensive review published recently Sundberg⁶⁰ described the inaccuracies in nickel analyses when significant quantities of ferric ion are present. In the case of the oxidized ore the additional uncertainty associated with Fe (III) is approximately 10%.

The gradual loss of weight of the sample during calcination (graph 18) may in part be due to the loss of entrained water. Such water loss would be expected to cause cracking and fissuring of the dunite grains thereby increasing the effective surface area accessible to the leaching solution. However, no visible evidence of such fissuring was obvious at low magnifications although the appearance of the dunite had changed from a pale glassy green colour to a deep red-brown.

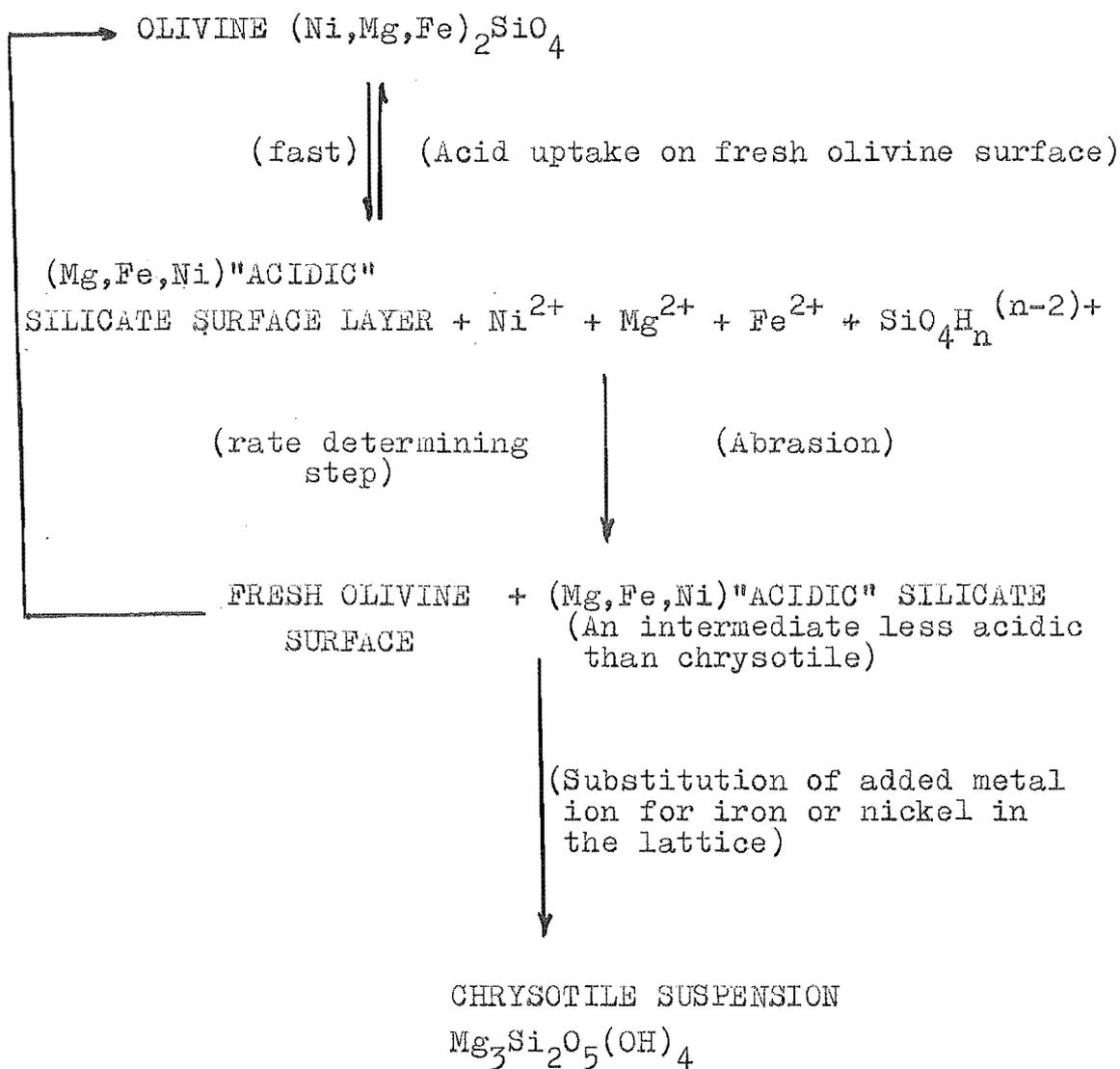
(b) Reductive Roasting. The next consideration was the behaviour of dunite under reducing conditions. The effect of reduction is to transform cations into the metallic state. Such a reduction is of little value if the iron, magnesium and nickel are equally affected and thus no element of selectivity is introduced. A more relevant consideration is the effect of EDTA solution upon the leaching of reduced dunite (i.e. will E.D.T.A. react selectively with elemental iron and nickel).

Reduction was carried out by heating the dunite with fine coaldust in a closed crucible over a Meker burner. The acid uptake (graph 19) and nickel release (graph 20) both increased relative to untreated ore but the yield of nickel per mole of acid consumed was reduced.

Acid leaching in the presence of E.D.T.A. (graphs 22 and 23) gave a similar result. There would appear to be no enhancement of the nickel release due to differentiation between elemental iron and nickel.

3.3 MODEL FOR THE DUNITE LEACHING PROCESS.

A possible model for the leaching process is as follows:-



The above model takes into account such experimentally observed effects as that of particle size, the addition of excess cation etc. Implicit in this model is that the acid leaching of dunite is a surface reaction only.

CHAPTER FOUR

CONCLUSION

The object of this research, as outlined in the abstract, was to undertake a general investigation of the acid leaching of dunite ore and further to examine the nature of the leaching reaction itself. The possibility of a two stage surface/lattice reaction has been suggested^{43,44} and the elucidation of such a reaction scheme is fundamental to any attempt to selectively leach nickel from the lattice. The former objective - to investigate the behaviour of dunite ore under the action of various leaching agents - has been attained satisfactorily. The latter question - as to whether the reaction proceeds by a simple surface reaction or otherwise - is not so easily answered. The idea of a secondary lattice reaction was not strongly supported by experimental data.

The shape of the leaching curve (page 41) an initial sharp slope breaking abruptly to a lesser constant slope may be satisfactorily accomodated in a purely surface reaction theory if one considers the change in slope to correspond to complete surface saturation and the secondary slope merely to reflect the rate of renewal of the raw dunite surface by the abrasive leaching slurry.

The existence of differences in "leaching efficiency" at various pHs (page 43) implies a degree of selectivity in the removal of nickel ions but whether this removal is from the dunite surface or from the dunite lattice is

indeterminate.

Similarly the effect of excess metal ion solutions as leaching agents (page 44) offers little real insight into the mechanism of the reaction. The fact that the effect cannot be enhanced or reproduced by addition of successive aliquots of metal ion suggest either surface saturation (if this is where the effect takes place) or a solubility effect (if the observed metal ion effect derives from a process occurring in solution).

Formation of a clino-chrysotile suspension (page 46) certainly indicates destruction of the dunite lattice which in turn implies surface reaction as does the first order relationship between particle size and rate of reaction (page 48).

The effect of complexing agents (page 48) (or rather the lack of effect) in selectively removing ions from the lattice is again evidence against a solid phase reaction.

The effect of oxidative roasting (page 52) however raises an interesting question. The iron (II) release is approximately independant of ore treatment - the iron (III) being released in the initial stages of the reaction - indicating either a lattice reaction or perhaps merely a replenishment of the unoxidized dunite surface by abrasion.

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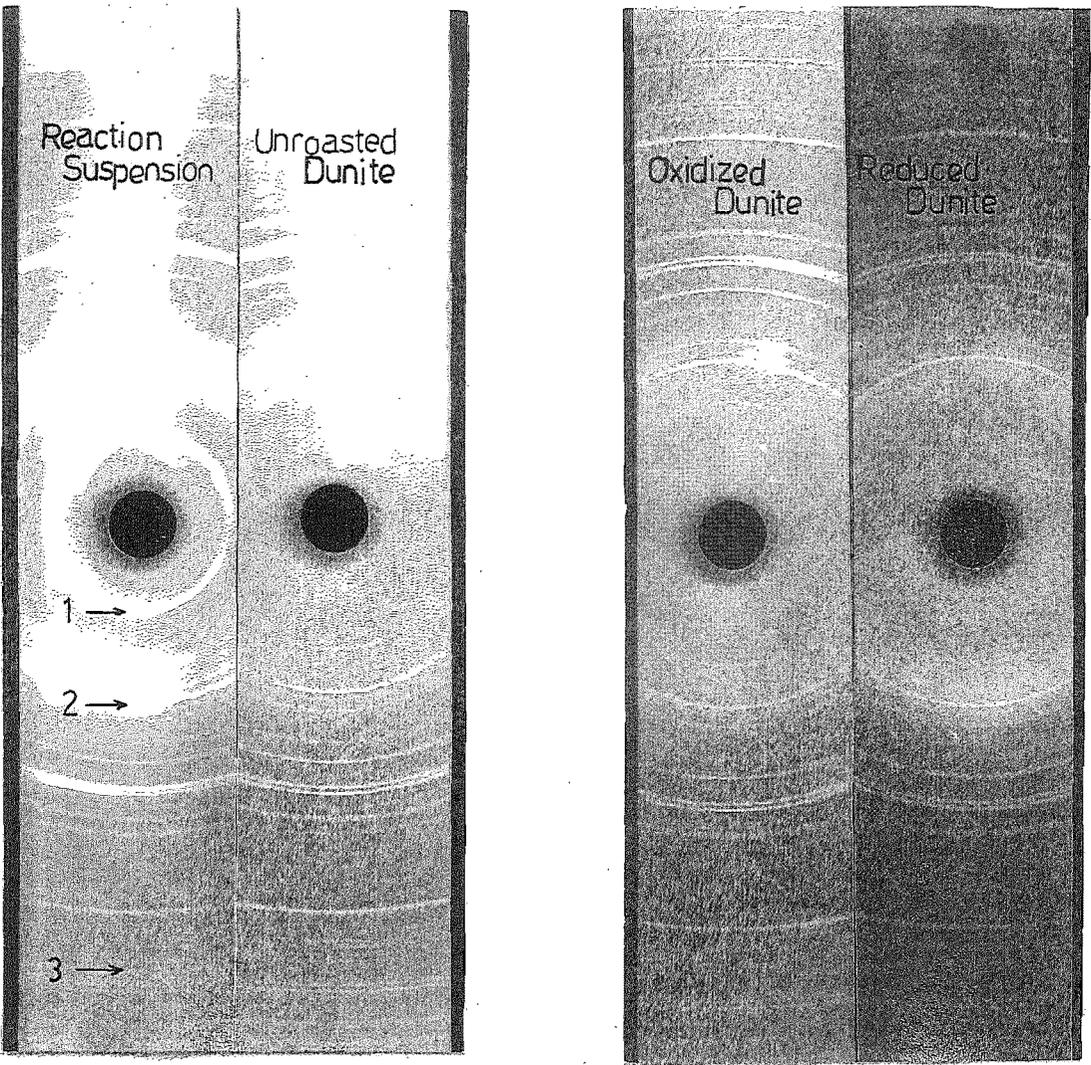


FIG. 2 X-RAY POWDER PHOTOGRAPHS OF SOLID STATE PRODUCTS AND REACTANTS.

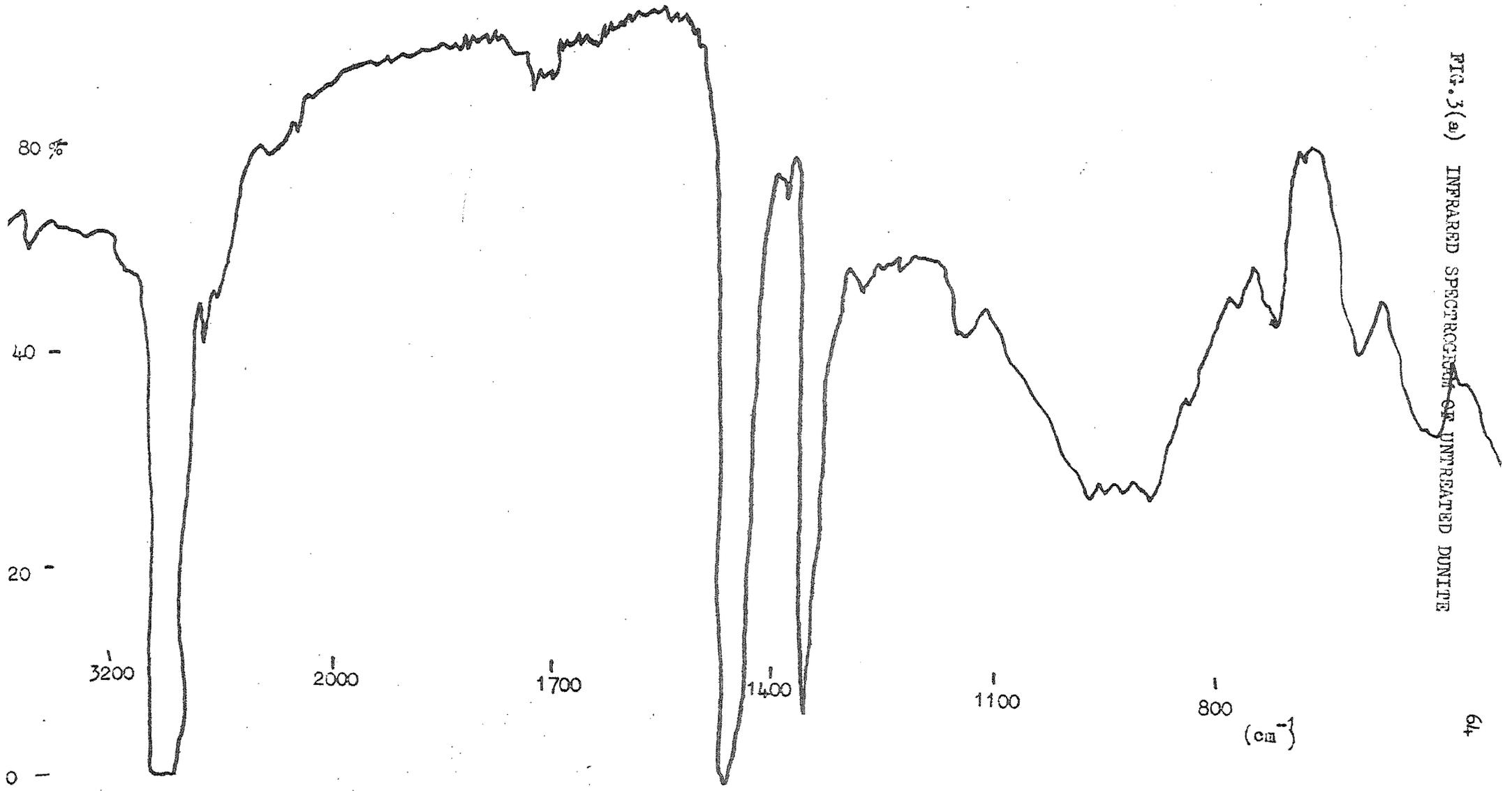


FIG. 3(a) INFRARED SPECTROGRAPH OF UNTREATED DUNITE

FIG. 3(b) INFRARED SPECTROGRAM OF OXIDIZED DINITRE

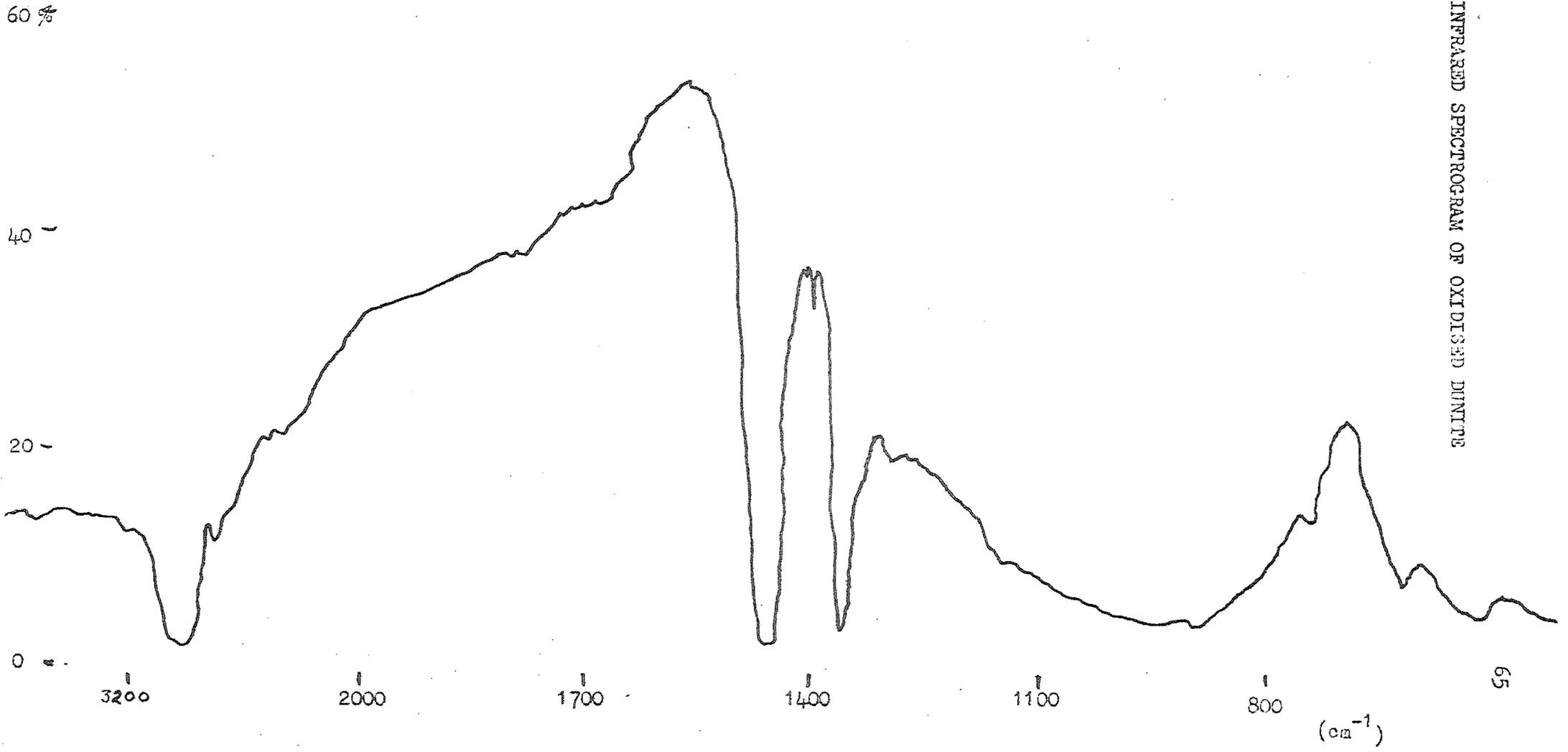
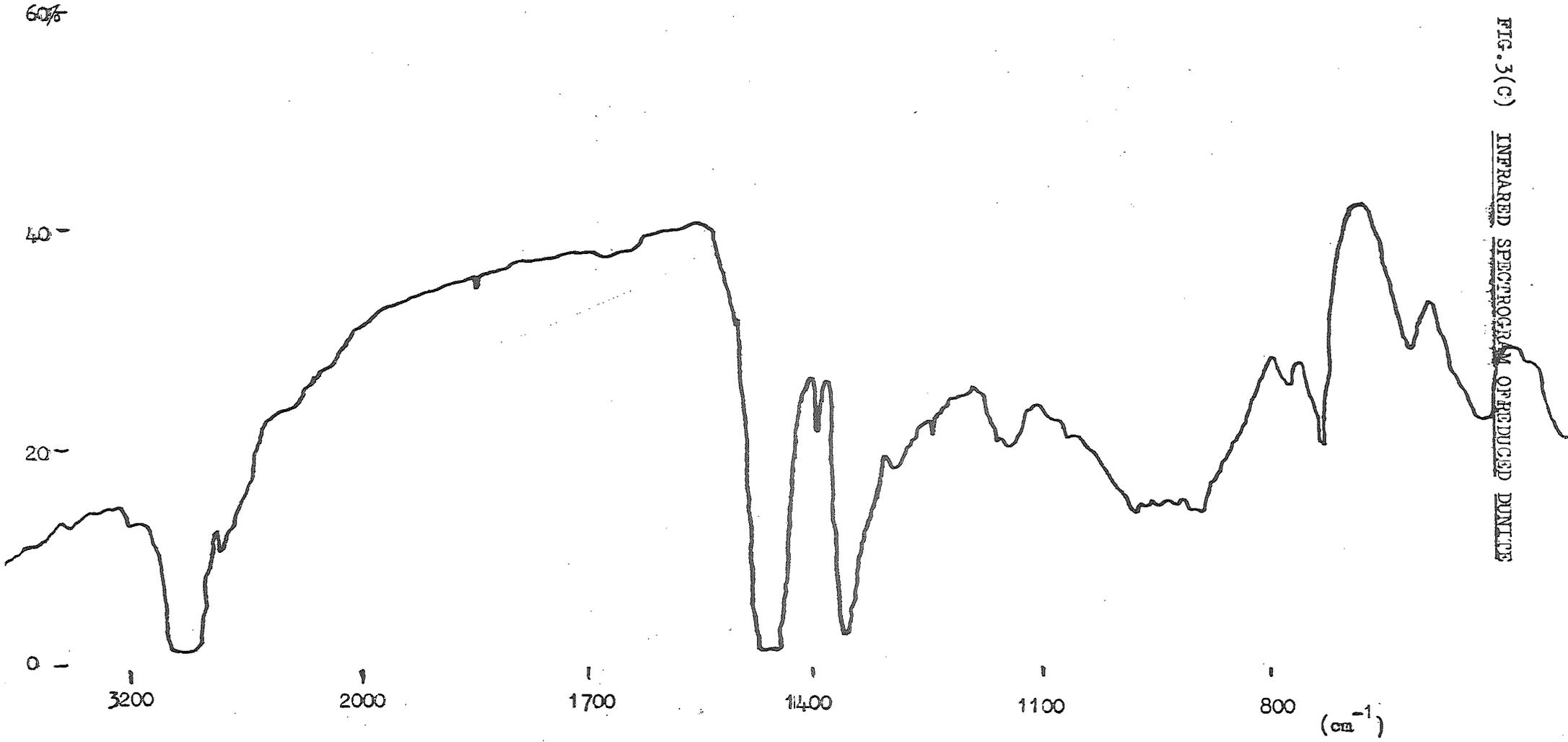


FIG. 3(C) INFRARED SPECTRUM OF REDUCED DUNITE



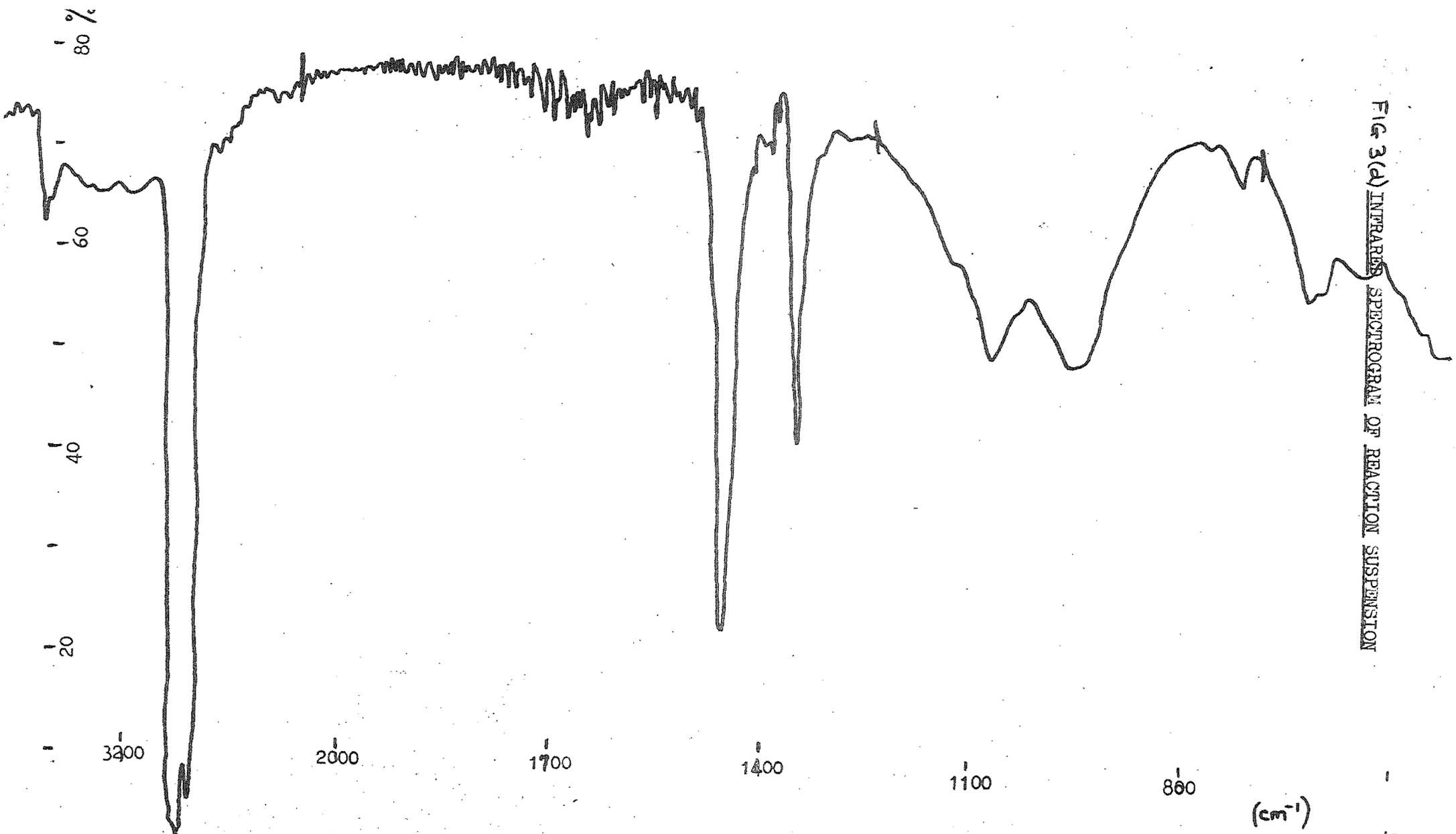


FIG 3(D) INFRARED SPECTROGRAM OF REACTION SUSPENSION