NICKEL HYDROXIDE RECOVERY FROM STAINLESS STEEL PICKLING LIQUOR BY SELECTIVE PRECIPITATION METHOD

A DISSERTATION
Submitted in partial fulfillment of the
requirements for the award of the degree
of
MASTER OF TECHNOLOGY
in
CHEMICAL ENGINEERING
(With Specialization in Industrial Pollution Abatement)

By
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CANDIDATE'S DECLARATION

I hereby declare that the work, which is being presented in the dissertation entitled **"NICKEL HYDROXIDE RECOVERY FROM STAINLESS STEEL PICKLING LIQUOR BY SELECTIVE PRECIPITATION METHOD"** in the partial fulfillment of the requirements of the award of the degree of Master of Technology in Chemical Engineering with specialization in Industrial Pollution Abatement, submitted in the Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee, is an authentic record of my own work carried out during the period from June 2005 to June 2006 under supervision of **Dr. B. Prasad**, Associate Professor, Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee.

I have not submitted the matter, embodied in this dissertation for the award of any other degree.

Date: June 30, 2006

Place: Roorkee

(P.DHANASEKARAN)

CERTIFICATE

This is to certify that the above statement made by the candidate is correct to the best of my knowledge and belief.

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(P.DHANASEKARAN)

ABSTRACT

Nickel removal from the pickling liquor is done by several methods, in that selective precipitation method is the new process. Before , pickling is done by hydrochloric acid and sulfuric acids but now pickling process carried out with concentrated hydrofluoric and nitric acid because of less waste and pollution forming. The treatment of stainless steel pickling waste is compulsory due to its toxicity and polluting character. Moreover, metals and acids recovery is interesting from an economical point of view. Spent pickling liquor classical disposal consists of high-pH neutralization with lime and potassium or sodium hydroxide. This process generates high wastes volume and valuable materials lost, so recovery processes have been developed. Free acid recovery processes do not regenerate HF or HNO_3 from metallic complexes in solution. However, acid retardation is the most implanted technique due to its low cost, although wastes volume is still high.

Selective precipitation method has several advantages than any other metal removing process because of it's high purity product formation and the excellent efficiency in the metal recovery. In selective precipitation method initially we are removing the chromium and Iron as filtercake.So that the effluents contains very pure nickel and it may remove by adding alkali .The main parameters influencing the nickel hydroxide precipitation are temperature,pH, alkali concentration. Based on this parameters nickel hydroxide concentration will vary. The metal hydroxide ageing time influence on its solubility and the eventual reasons of such influence are of particular interest. Recent investigations were conducted with nickel hydroxide precipitate. Its solubility in neutral water is highly dependent on a solution pH .

Several experiments are carried out with the different nickel and other metal concentrations with the alkali solutions and the purity of effluents after filtrations were studied.

Parameters are changed and concentrate on the nickel recovery and it's purity.Optimum conditions were reached from different experimental results.

The chemical properties of the stainless steel pickling liquor and hydroxide sludges have been investigated through chemical analysis, X-ray diffraction analysis, particle size distribution, scanning electron microscopy and thermal analysis.

The basic principles of selective precipitation method are;
Metals other than nickel is precipitated initially and those leaves the nickel alone in the effluent as liquid phase.
Selective levels of Temperature,pH,alkali concentration changes the precipitation capability of the effluent coming after the removal of other metals.

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NOMENCLATURE

$F_{Ni\ Out}$ - Steady state mass flow of Nickel exiting the reaction vessel (g/l)

$F_{Ni\ In}$ - Steady state mass flow of Nickel entering the reaction vessel (g/l)

SPL - Spent Pickling Liquor

SH - Sodium Hydroxide

KF - Potassium Fluoride

HF - Hydrofluoric acid

IR - Infra Red

PXRD - Powder X-Ray Diffraction

WH - Weak hydroxide

AAS - Atomic Absorption Spectrophotometer

OSHA - Occupational Safety and Health Administration

ERC - Emergency Response Center

CHAPTER 1

1.1 INTRODUCTION

Mankind has used metals for several millenniums and in our day the mass usage of metals is accepted as an inalienable fact. Metals do have a fundamental weakness, bulk usage of metals causes environmental damage. Thus there have been demands for the use of alternative materials. However, there is much scope to make environmental improvements to the production and use of metals. The hydro metallurgic industry produces many types of waste streams. Increasing costs and stricter regulations require more effective methods for cleaning these wastes. One of the most important tasks is the removal or recovery non-ferrous metals from effluents. The effective recovery of these metals is possible only if the separation process is selective enough.

Especially in small scale industries operating in communal areas there is the need to find easy and reliable methods for waste treatment. When waste effluents are released through a sewerage system to municipal sewage disposal plants the metal releases accumulate in the sludge which limits the profitable use of the sludge as a fertilizer or land filling material. The aim of this work was to study and develop effective and economical recovery of Nickel hydroxide, which as waste in the metal finishing industry. Nickel was discovered some 250 years ago. It is a metallic element and the fifth most abundant after iron, oxygen, silicon and magnesium. Links to certain serious illnesses have been recognised for over 100 years and controlled through significant steps taken to minimise occupational exposure through process improvement (Peter H. Kuck).

Nickel is plentiful and over a million tonnes is produced each year worldwide by mining, milling, smelting and refining operations. However, it is also one of the most recycled materials in today's global economy. Add to that the fact that most nickel containing products have a long service life – on average over 25 years – and you have a substance that makes a major contribution towards sustainable development.

Hydroxide precipitation is the standard method for removing harmful metals from metal finishing wastewater. This is achieved by adjusting the pH of the wastewater with an alkaline reagent to deposit the dissolved metals and settle and remove the resultant metal hydroxide precipitates.

Heavy Metals - Metals, when in significant concentrations in water that may pose detrimental health effects. Heavy metals include lead, silver, mercury, copper, nickel, chromium, zinc, cadmium and tin that must be removed to certain levels to meet discharge requirements.

Metal Hydroxides - When caustic is added to water containing heavy metals, a metal hydroxide solid or precipitate is formed.

1.2 NICKEL HYDROXIDE PHYSICAL PROPERTIES

Nickel hydroxide ($Ni(OH)_2$) is insoluble in water but soluble in acids and ammonia. When dissolved in ammonia it forms complexes. It is used as electrode material for secondary cells (Environmental Protection Planning And Standards).

TABLE 1.1 Physical properties of nickel hydroxide

Name	Chemical formula	Relative molecular mass	Appearance	Density (g/cm^3)	Melting point (°C)	Boiling point (°C)	Solubility (water;other solvents)
Nickel hydroxide	$Ni(OH)_2$	92.72	green powder	-	decomposes above 200	-	insoluble; soluble in acids and ammonia

TEM image of the $Ni(OH)_2$ powder is shown in Fig1.1. TEM investigation showed that it is in good crystallinity(Masahiko ITO,Rinso TACHIBANA).

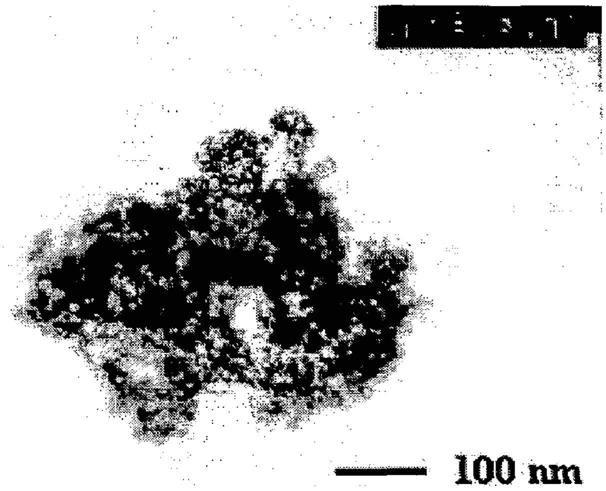


Fig.1.1 TEM image of $Ni(OH)_2$ powder.

Note: transmission electron microscopy (TEM)

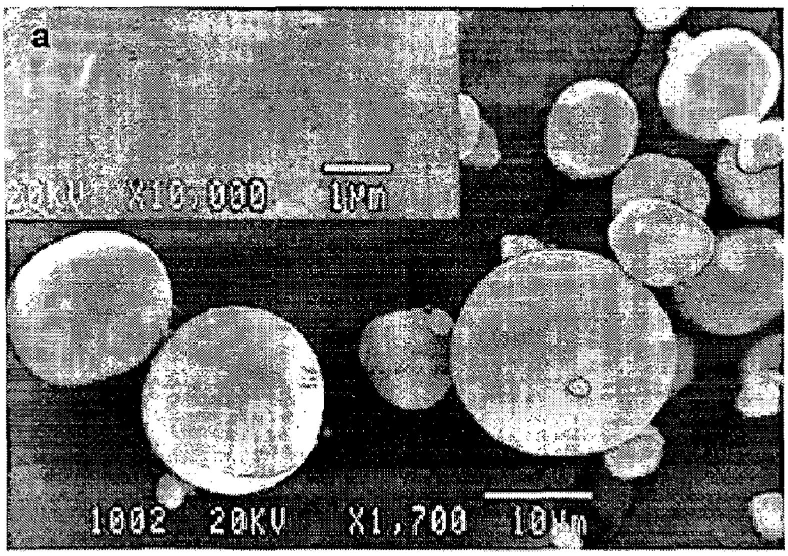


Fig.1.2 (a) SEM micrograph of coated $Ni(OH)_2$

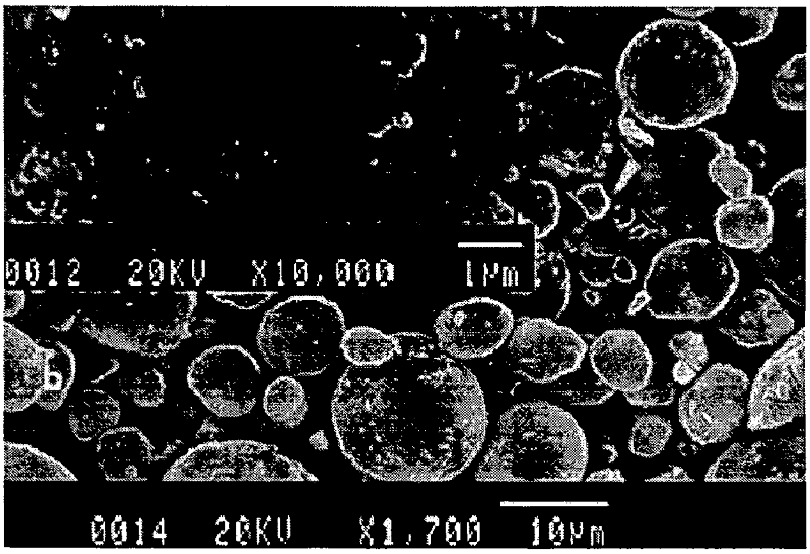


Fig.1.2 (b) SEM micrograph of uncoated $Ni(OH)_2$

SEM images of the uncoated and coated nickel hydroxide particles Fig1.2 a & b. A high resolution SEM image was inserted in each case to further observe the surface morphology and particle size. In Fig1.2(b).the surface exhibited numerous sheet-like particles with a size of 500–1000 nm. These small sheet-like particles are aggregated together on the surface of nickel hydroxide particles. Compared to the coated sample, the surface of uncoated spherical nickel hydroxide particles seems smooth, as shown in Fig.1.3. This indicates that the chemical coating (Taokai Ying).

The weight loss and corrosion potential of oxidized and blank stainless steels pickled in HF are shown in Fig1.3. The weight loss of oxidized stainless steel increases rapidly at the beginning due to the dissolution of metals and, as before, the undercut oxide scales (Fig.1.3). After about 70s, the increase in weight loss is significantly suppressed.

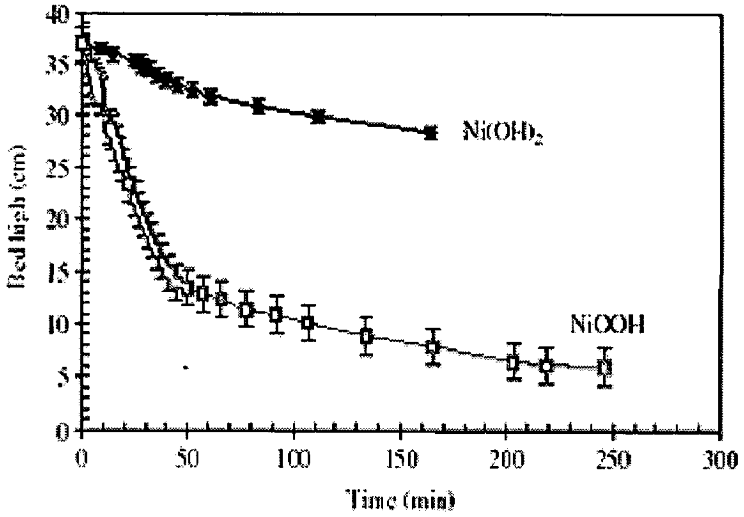


Fig.1.3 Setting characteristics of $Ni(OH)_2$ precipitate formed from equal initial mass of Ni(10g) at precipitation pH (10) for $Ni(OH)_2$

1.3 HEALTH EFFECTS BY NICKEL AND NICKEL COMPOUNDS

Nickel contributes in many ways to the health of people and environments. It is, as well, an essential element for plants, some animals and perhaps for humans. It can, however, have toxic effects in certain circumstances and at certain dosages. Very small amounts of nickel have been shown to be essential for normal growth and reproduction in some species of animals; therefore, small amounts of nickel may also be essential to human.

Workers inhalation of nickel refinery dust, which contains nickel subsulfide, has resulted in increased numbers of deaths from lung and nasal cavity cancers, and possibly cancer of the voice box. The nickel compounds implicated as potential carcinogens are insoluble dusts of nickel subsulfide and nickel oxides, the vapor of nickel carbonyl, and soluble aerosols of nickel sulfate, nitrate, or chloride. Evidence for the carcinogenicity of nickel metal and other compounds is relatively weak or inconclusive (Environmental Protection Planning And Standards)

The most common adverse effects of nickel exposure are skin allergies, specifically dermatitis. Rhinitis, nasal sinusitis, and nasal mucosal injury are among the effects reported in workers chronically exposed to nickel compounds. Asthma has been reported in nickel platers exposed to nickel sulfate, and in welders exposed to nickel oxides.

The lung is the target organ for nickel toxicity in humans. After comparing ambient air nickel levels with nickel levels in work places associated with adverse effects, EPA has concluded, "human health effects other than cancer appear to be limited to the occupational environment."

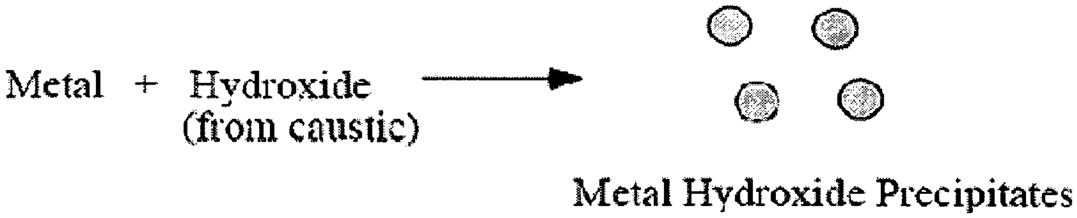
An environmental risk assessment requires an analysis (effect assessment) to be conducted to determine the "safe" level of nickel in the environment. This is called the predicted no effect concentration (PNEC[1]). This value is compared with the predicted environmental concentration (PEC[2]) which is part of the exposure assessment (*N.J. Sanders*).

The PEC is divided by the PNEC and if the resulting risk characterization ratio (RCR) is > 1, risk to the environment is assumed. This analysis is conducted for water-dwelling organisms, sediment-dwelling organisms, soil-dwelling organisms, and microorganisms in sewage treatment plants. The scientific basis of the risk assessment evolves from the premise that the nickel ion is the putative toxic agent.

OSHA issues permissible exposure limits for nickel and soluble nickel compounds. Under the Emergency Planning and Community Right-to-Know Act, release of more than one pound of nickel and nickel compounds into the air, water, and land must be reported annually and entered into the national Toxic Release Inventory (MSDS of Pickling liquor)

1.4 METAL TREATMENT BY HYDROXIDE PRECIPITATION

As metals enter the treatment process, they are in a stable, dissolved aqueous form and are unable to form solids. The goal of metals treatment by hydroxide precipitation is then to adjust the pH (hydroxide ion concentration) of the water so that the metals will form insoluble precipitates. Once the metals precipitate and form solids, they can then easily be removed, and the water, now with low metal concentrations, can be discharged. Metal precipitation is primarily dependent upon two factors: the concentration of the metal, and the pH of the water. Heavy metals are usually present in wastewaters in dilute quantities (1 - 100 mg/l) and at neutral or acidic pH values (< 7.0). Both of these factors are disadvantageous with regard to metals removal. However, when one adds caustic to water which contains dissolved metals, the metals react with hydroxide ions to form metal hydroxide solids:



High pH values correspond to high hydroxide concentrations. Visual representations of the pH values that promote metal precipitation are displayed in the fig1.4. Figure illustrates that how the solubility of a Nickel metal is directly controlled by pH. The y-axis displays the concentration of dissolved metal in the wastewater, in mg/l. Notice the wide variation in scale. The upper part of the scale shows a dissolved concentration of 100 mg/l. The lowest number on the scale is 0.001 mg/l. These solubility graphs display regions where the metals are soluble or insoluble. The region above the dark lines (the shaded areas) for metal signifies that the metal should precipitate as metal hydroxides. This is referred to as the precipitation region. The region below or outside of the dark lines illustrates where the metals are dissolved in solution, no precipitation occurs, and no metal removal takes place (Peter Caenen, Mathieu Daerden,David Vaes).

Thus, simply adjusting the pH from 6.8 to 8.6 has effectively precipitated most of the dissolved metal from the water. Since all metals display similar effects, it is clear that the adjustment of pH is critical when the metal is to be removed from the waste water Some variations in the exact values of the metal concentrations will occur due to the presence of other substances in the wastewater.

Compounds such as cyanide or ammonia can inhibit precipitation of metals, and limit their removal to the point where discharge limits can be exceeded. Also, note that not all metals have the same minimum solubility. Therefore in a wastewater where multiple metals are present, as a general rule, pH should be adjusted to an average value, approximately 9.

1.5 NICKEL HYDROXIDE USES

Nickel hydroxide is widely used as the positive electrode material in nickel batteries of MH–Ni, Cd–Ni, Fe–Ni and Zn–Ni secondary alkaline batteries with characteristics of high power density, excellent cyclability, high specific energy and low toxicity the precipitation of nickel hydroxide by alkali addition is not very selective or without processing difficulties. Therefore, conditions must be optimized to reduce impurity uptake and improve settling characteristics. Little information is given about the conditions of the $Ni(OH)_2$ precipitation step. A number of patents and studies were performed; however, the procedures showed great variability in working pH and temperature(Environmental Protection Planning And Standards).

1.6 SOLUBILITY MEASUREMENTS OF $Ni(OH)_2$

The solubility of nickel hydroxide as a function of pH at various temperatures is crucial to define the operating window in which to control precipitation. It is well known that the solubility of recent investigations were conducted with nickel hydroxide precipitate. Its solubility in neutral water is highly dependent on a solution pH with a minimum value of pH 10, at which it falls to 10^{-3} mg/dm^3 .

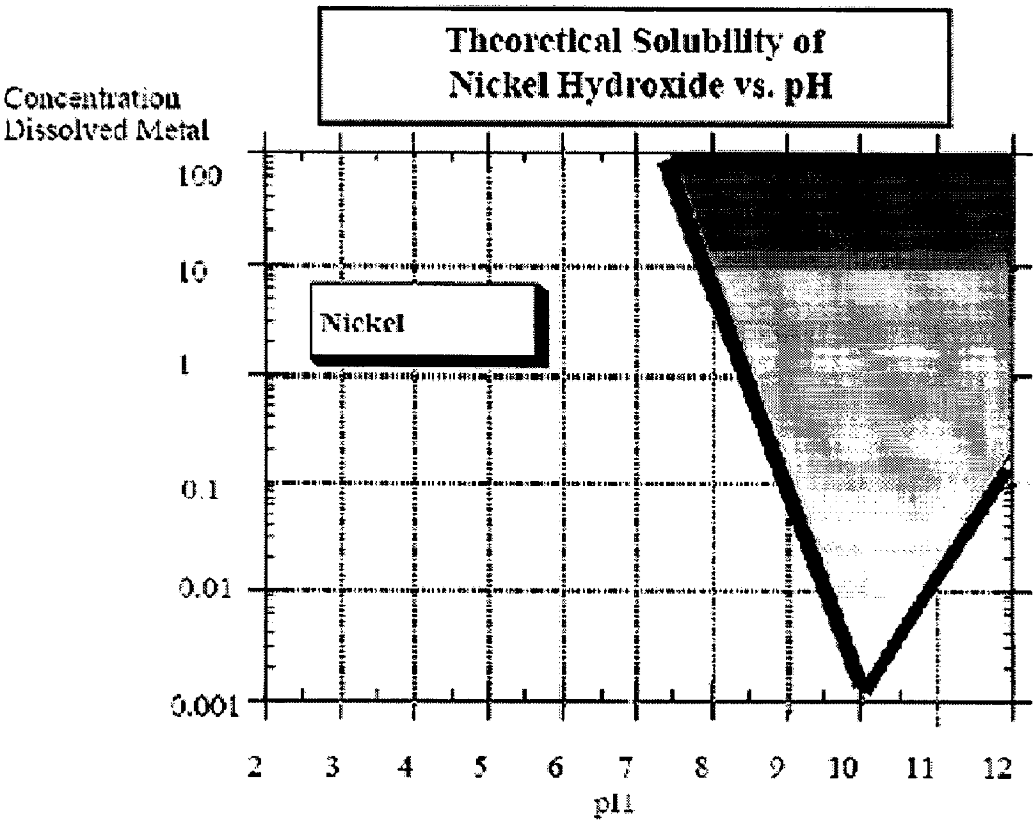


Fig.1.4 Nickel solubility Graph

1.4 NICKEL HYDROXIDE PRECIPITATION MECHANISM

Sample preparation

Nickel hydroxide samples were prepared in separate flasks by dissolving 12.8182 g (first series) or 1.2818 g (second series) of nickel chloride ($NiCl_2 \cdot 6H_2O$) in 150 cm^3 of distilled water and by adding dropwise 10% solution of NaOH until pH 11 was attained. Hence, each flask of the first series contained 5 g, while each one of the second series contained 0.5 g of nickel hydroxide. Nickel hydroxide has a low solubility product (1.6×10^{-14}) and is therefore prepared by alkali-induced precipitation from a suitable nickel salt solution. Several factors govern the outcome of a precipitation reaction. Important among these are:

(i) pH at precipitation;
(ii) choice of alkali;
(iii) temperature of the reaction;
(iv) choice of the nickel salts; and
(v) rate of mixing of the reactants.

As in any precipitation reaction, the freshly precipitated nickel hydroxide is digested by ageing in mother liquor, or neutral wash solution or by hydrothermal treatment. Digestion enables crystal growth. Any change in the precipitation conditions affects the structure, composition and morphology of nickel hydroxide with a profound and often unpredictable impact on the reversible charge-storage capacity. Nickel hydroxide precipitation begins at pH = 5.5–6.

All nickel hydroxide samples were characterized by wet chemical analysis to arrive at an approximate formula. The Nickel content was estimated by the DMG method. The OH^- content was estimated by dissolving a known weight of the sample in excess of acid and back titrating the excess against a standard NaOH solution using a pH meter. Bonding in nickel hydroxide is anisotropic. While intralayer bonding is strongly iono-covalent in nature, bonding between layers is of the weak van der Waal's type. The layers therefore tend to lose orientation with respect to each other and this results in disorder. The orientation of layers is affected by the precipitation conditions and hence it is important to explore different regimes of pH, concentration and temperature, as well as the conditions of digestion.

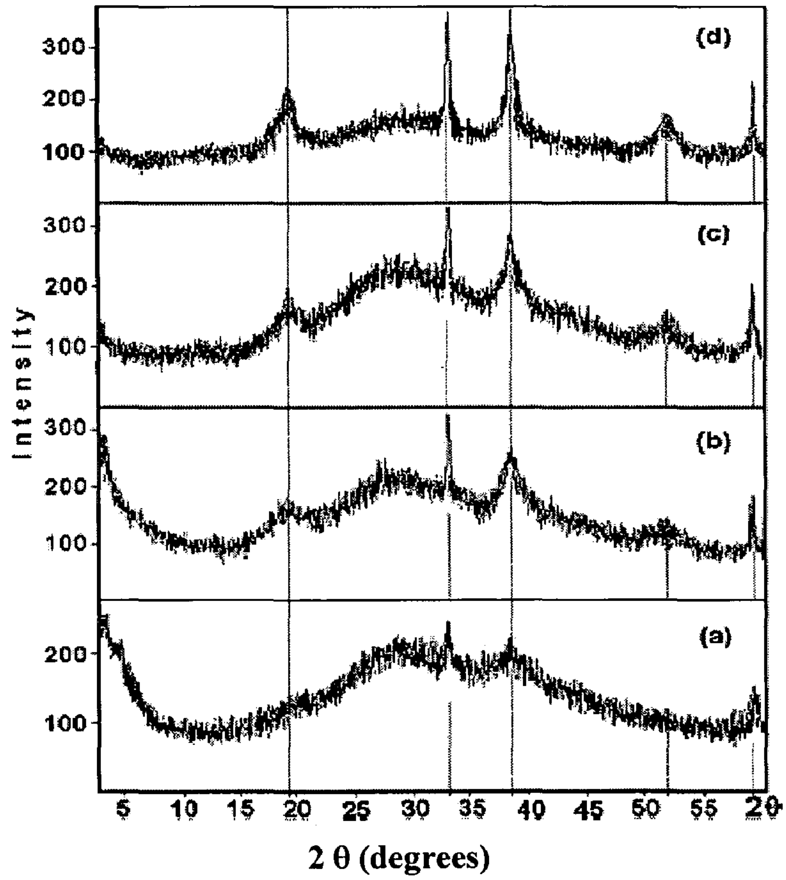


Fig.1.5 X-ray patterns of $Ni(OH)_2$: (a) freshly settled; (b) after 1 month storage; (c) after 2 months storage; (d) after 3.3 years storage.

Samples with such prepared nickel hydroxide suspensions were used for further examinations either at once (freshly settled nickel hydroxide) or after storage over the mentioned time periods. The resultant samples were examined for crystallinity and solubility: (a) freshly settled and investigated the same day (without storage); (b) after 1 month;(c) after 2 months;(d) after 3.3 years storage (for X-ray examinations)(Malgorzata, Tadeusz, Dominik)

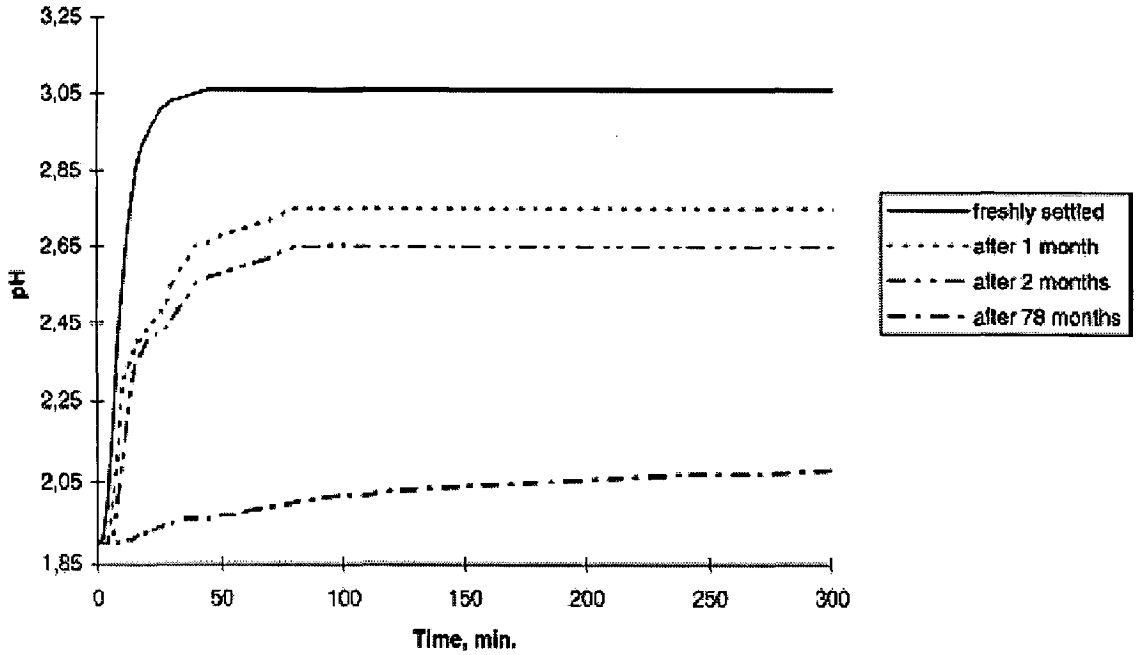


Fig.1.6 pH changes in $Ni(OH)_2$ suspension in water acidified to pH 1.9 as a function of time for nickel hydroxide species: freshly settled, stored during 1, 2 and 78 months (6.5 years).

Sodium hydroxide-induced precipitation

Precipitation at constant low pH

Nickel salt solutions tend to be acidic (pH≈3) and on the addition of strong alkali, precipitation takes place at pH = 5.5–6. Terminating alkali addition at pH = 7 yields a sample obtained at a constant 'low pH'. Addition of excess alkali creates the possibility of the interaction of nickel hydroxide with OH^- in solution. Although nickel hydroxide is generally not known to be amphoteric, this interaction appears to affect the structure of the product. In separate experiments, the alkali addition was stopped at final pH values of 7, 9 and 12, respectively, to study the effect of pH on the product. These samples were labeled 7SH, 9SH and 12SH **(SH: sodium hydroxide),** respectively (T.N. Ramesh, P. Vishnu Kamath).

The PXRD patterns of 7SH and 12SH samples obtained by strong alkali precipitation at pH 7 and 12, respectively, are shown in Fig 1.6. The *d*-spacing of 7SH appear at values expected for-$Ni(OH)_2$, but the peaks are non-uniformly broadened. The first peak at 4.64A° ($2\theta = 19.1°$) corresponds to inter-layer separation in $Ni(OH)_2$. The (h k 0) peaks, i.e.,(1 0 0) and (1 1 0) are the narrowest, whereas the (h 0 0), and (0 0 1) peaks are considerably broadened. The PXRD pattern of 9SH is similar and therefore is not shown. The high angle (>30° in 2θ) reflections in the PXRD pattern of 12SH appear at positions expected for the $Ni(OH)_2$ phase, but the first reflection is poorly defined on account of excessive broadening and due to the appearance of an additional feature. There are two maxima at 5.3 °A (16.7° in 2θ) and 4.64 °A (19.1° in 2θ). Such a pattern was originally ascribed to a phase, which is neither nor, but more recently has been attributed to the interstratification (T.N. Ramesh, P. Vishnu Kamath).

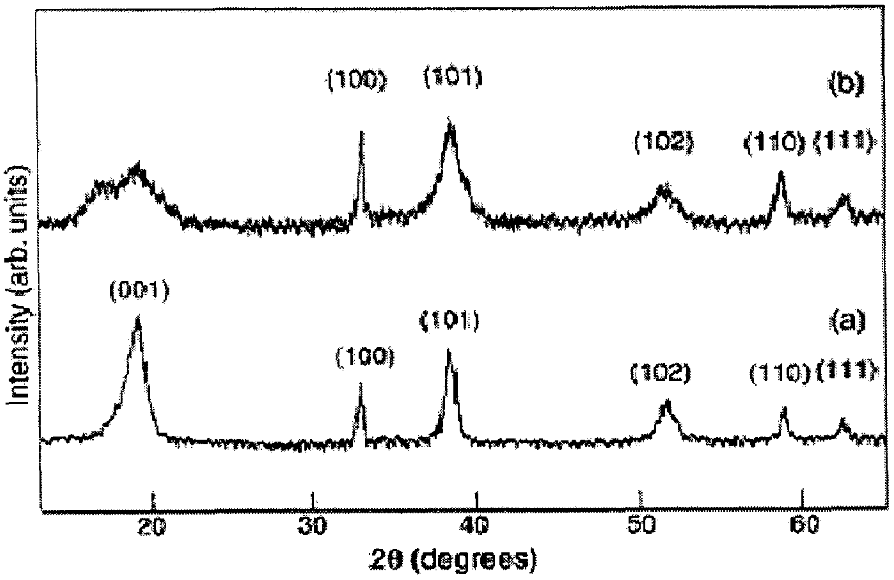


Fig.1.7 PXRD patterns for (a) 7SH and (b) 12SH nickel hydroxide samples.

Note: powder X-ray diffraction (PXRD)

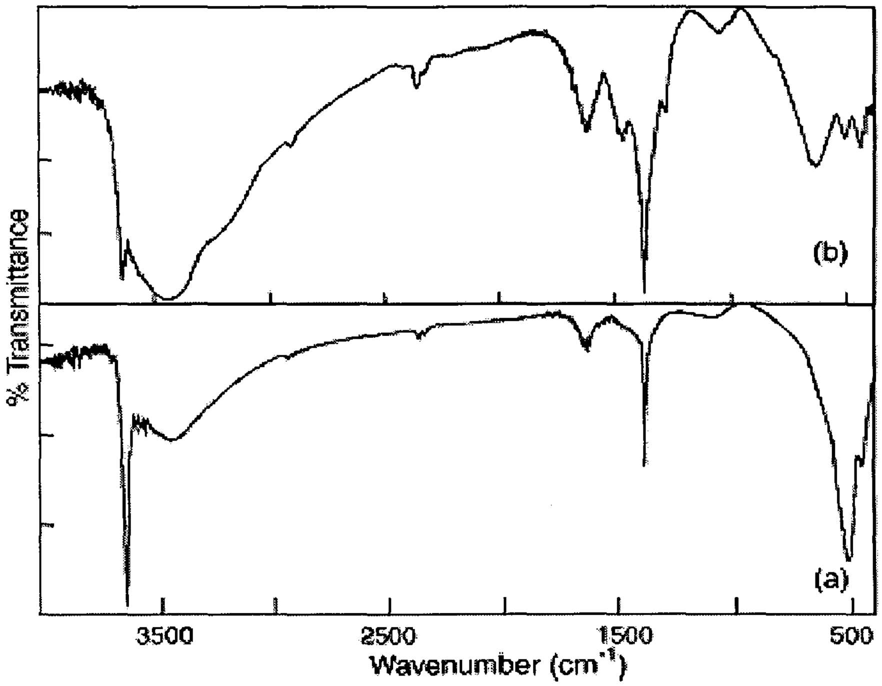


Fig.1.8 Infrared spectra for (a) 7SH and (b) 12SH nickel hydroxide samples of motifs in the matrix of $Ni(OH)_2$.

The IR spectrum of 7SH shows(Fig 1.8) only three absorptions: (i) a 3650 cm^{-1} peak due to non-hydrogen bonded OH groups; (ii) an in-plane NiOH bending vibration at 520 cm^{-1}; (iii)NiO stretching at 460 cm^{-1}.The sharp peak at 1388 cm^{-1} is due to adsorbed nitrates. In addition to these absorptions, the spectrum of 12SH shows peaks due to (i) hydrogen-bonded OH stretching at 3450 cm^{-1}(ii) intercalated nitrate ions in the wave number region 1600–1100 cm^{-1}; (iii) blue-shifted NiOH bending vibration at 640 cm^{-1}. These are characteristic of the nickel hydroxide motifs (T.N. Ramesh, P. Vishnu Kamath).

Precipitation at constant high pH

Precipitation at a constant high pH can be carried out by the addition of nickel nitrate to a reservoir containing NaOH taken in excess. The PXRD pattern of the resultant product is given in Fig 1.9 & Fig1.10.

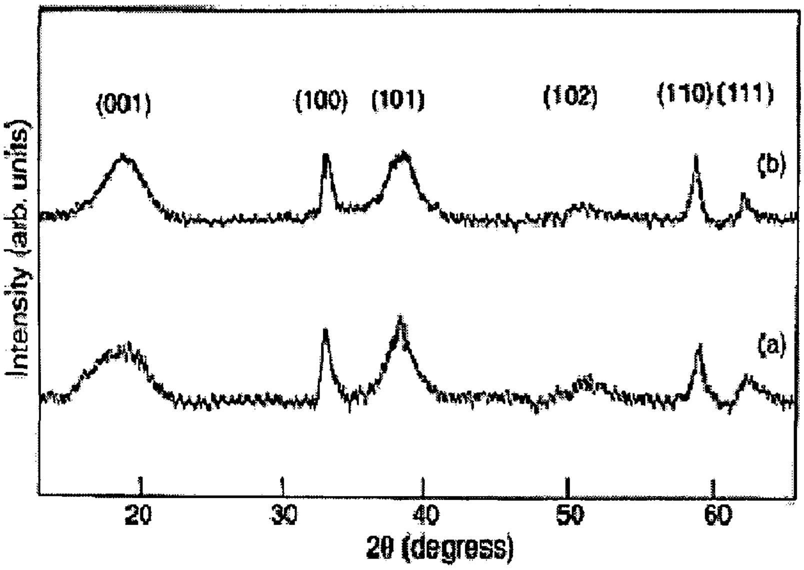


Fig.1.9 PXRD patterns for (a) 13SH25 and (b) 13SH80 nickel hydroxide samples.

Note: powder X-ray diffraction (PXRD)

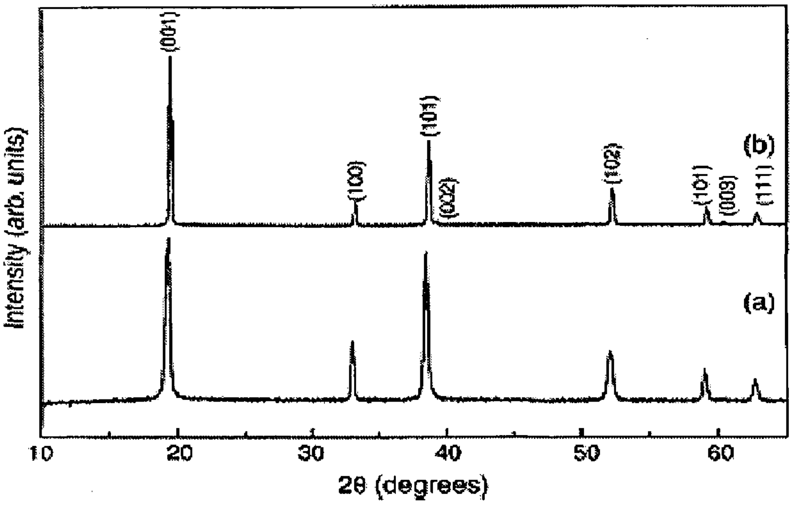


Fig.1.10 PXRD patterns for (a) 13SH170 and (b) CA200 nickel hydroxide samples.
Note: powder X-ray diffraction (PXRD)

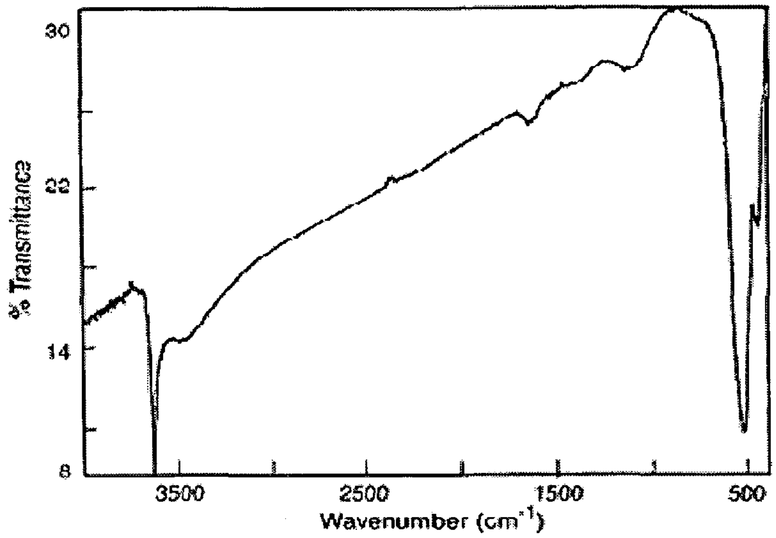


Fig.1.11 Infrared spectrum of the CA200 nickel hydroxide sample.(0 0 3) reflections (39° and 60.44° in 2*θ*).

The IR spectrum of the CA200 sample shown in Fig 1.11. is the one ideally expected for-Ni$(OH)_2$ .The crystallinity of the product is adversely affected on using a non-nitrate source. The PXRD pattern of nickel hydroxide obtained from nickel sulfate is given in Fig. and that for the product obtained from a reaction of NAS with a stoichiometric requirement of NaOH (final pH = 8.2) in Fig. This latter sample is X-ray amorphous. The IR spectrum is presented in Fig, and it exhibits all the features (T.N. Ramesh, P. Vishnu Kamath).

CHAPTER-2

LITERATURE REVIEW

T.N. Ramesh, P. Vishnu Kamath (2005) "Synthesis of nickel hydroxide: Effect of precipitation conditions on phase selectivity and structural disorder".

The synthesis of nickel hydroxide by precipitation from a suitable solution containing dissolved Ni^{2+} ions is described. A large matrix of precipitation conditions is explored to generate a wide range of nickel hydroxide samples. While most precipitation reactions result in the formation of-nickel hydroxide, the samples differ from one another in the degree of structural disorder as reflected by the differences in their powder X-ray diffraction (PXRD) patterns. A correlation of the long-range structure as deduced from diffraction studies with the short-range structure as deduced from infrared (IR) spectral studies is performed. The aim is to control the synthesis conditions to obtain materials with 'tailor-made' structural disorders.

Nickel hydroxide has a low solubility product (1.6×10−14) and is therefore prepared by alkali-induced precipitation from a suitable nickel salt solution. Any change in the precipitation conditions affects the structure, composition and morphology of nickel hydroxide with a profound and often unpredictable impact on the reversible charge-storage capacity.

Strong alkali induced precipitation

Nickel hydroxide samples were precipitated by the addition of NaOH(2M) solution to a solution of nickel nitrate (1M) at ambient temperature (28–30°C) using a Metrohm Model 718 STAT Titrino operated in the pH-stat mode. Nickel hydroxide precipitation begins at pH = 5.5–6. In separate experiments, the alkali addition was stopped at final pH values of 7, 9 and 12, respectively, to study the effect of pH on the product. These samples were labeled 7SH, 9SH and 12SH (SH: sodium hydroxide), respectively.

Ammonia-induced precipitation

Ammonia-induced precipitation at low temperature (4°C), WH4, yields a poorly ordered nickel hydroxide, while at high temperature (25–65°C), $Ni(OH)_2$ is obtained with a surprisingly high degree of crystallinity . The PXRD pattern of WH4(Fig2.1) is characteristic of a material with turbostratic disorder .The two high-angle reflections are accordingly indexed to reflect the two-dimensional ordering of nickel hydroxide sheets. The low-angle reflection appearing at 7.6 °A corresponds to the inter-layer spacing in nickel hydroxide. The IR spectra also reflect the dramatic changes brought about by the change in temperature (.WH4 exhibits all the characteristic absorptions of nickel hydroxide, while WH25 shows the features of $Ni(OH)_2$.

When nickel hydroxide (WH4) is aged in concentrated ammonia at ambient temperature, it transforms into crystalline $Ni(OH)_2$ (see Fig2.1. for the PXRD pattern of a partially-transformed sample). On ageing in concentrated alkali (6M KOH), it transforms into β_{bc} nickel hydroxide (Fig.2.1). This clearly shows that the pH during ageing has a profound affect on structural disorder. Fig 2.1. PXRD pattern of (a) WH4 sample compared with that of (b) WH25 sample. **Note; WH- weak hydroxide**

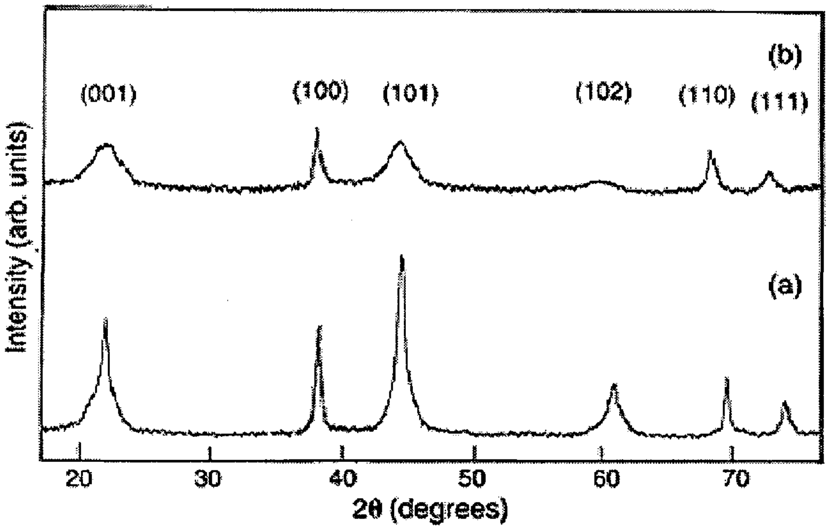


Fig.2.1 PXRD pattern of (a) WH4 sample compared with that of (b) WH25 sample Note; WH- weak hydroxide Disorder→Order transformation in nickel hydroxide system

Precipitation of a solid takes place when two solutions having different free energies are mixed. According to Ostwald's law, the solid obtained immediately on precipitation is not only disordered but also thermodynamically unstable with a free energy close to that of the reactants. The disordered phase transforms into a more stable phase of lower free energy in a step-wise manner. During the precipitation of nickel hydroxide, especially at low temperatures and moderate pH conditions as obtained during ammonia induced precipitations or stoichiometric strong alkali addition, the solid formed immediately on precipitation is the amorphous phase (Fig 2.2). This phase is metastable and transforms into other phases of progressively greater order and thermodynamic stability.

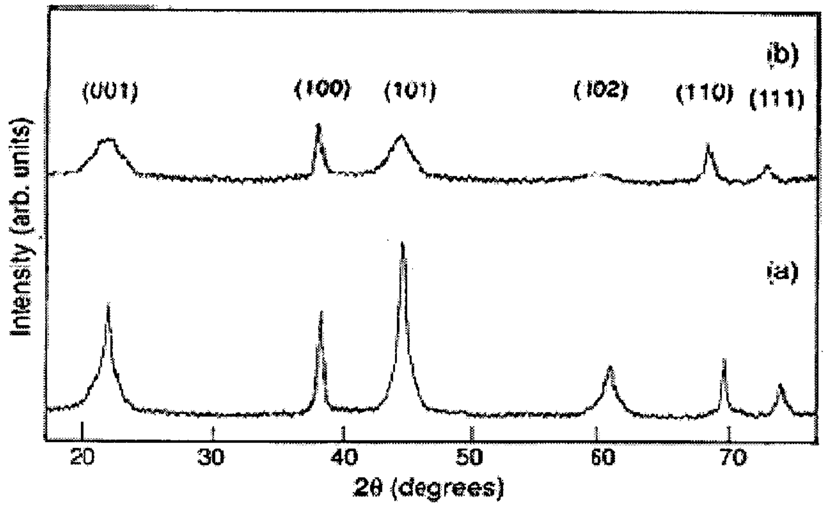


Fig. 2.2 PXRD pattern for WH4 sample aged in (a) 27% (w/v) NH_3 6M KOH for 15 days.

The dissolution–reprecipitation reaction is driven by free energy changes at the solid solution interface (Fig 2.3). The surface layers of β_{bc} nickel hydroxide interact strongly with the solution and their contribution to the free energy of the crystallite is small. This is especially true in instances where the nickel coordination is either incomplete or asymmetric as in the case of interstratified and hydroxyl-deficient samples. The surface layers therefore dissolve. When they reprecipitate, the slow kinetics leads to better crystallization and the surface layers are strongly bound to the ordered crystallite so that their contribution to the free energy of the crystallite exceeds the strength of interaction with the solution (Fig 2.3). For similar reasons, the inter-diffusion method, as well as the removal of ammonia method, leads to the formation of crystalline samples.

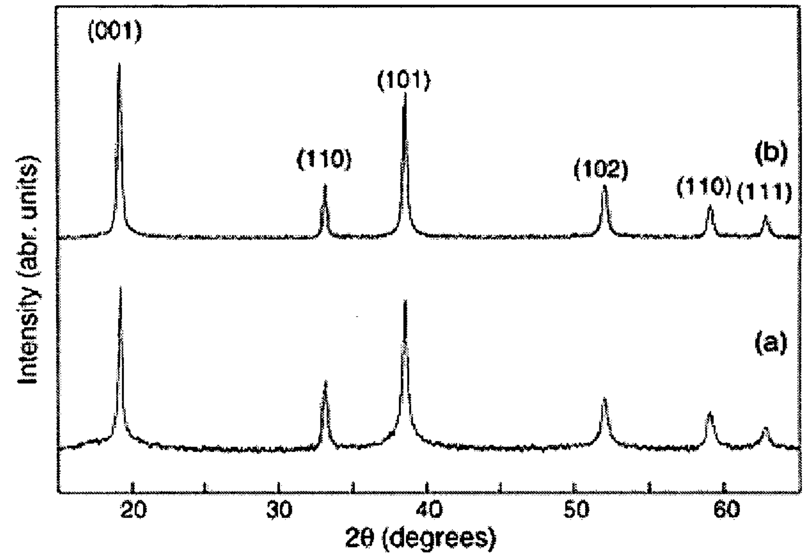


Fig.2.3 PXRD patterns for nickel hydroxide samples obtained by (a) removal of ammonia and (b) diffusion methods.

In the former method, ammonia has been introduced slowly with the object of forming the nickel ammine complex in site followed by hydrolysis. The latter method starts from the complex and facilitates precipitation by controlled decomposition of the complex by the slow removal of ammonia.

The metal hydroxide ageing time influence on its solubility and the eventual reasons of such influence are of particular interest. Recent investigations were conducted with nickel hydroxide precipitate. Its solubility in neutral water is highly dependent on a solution pH with a minimum value of pH 10, at which it falls to 10^{-3} mg/dm^3. In order to obtain more precise measurable nickel ion concentrations, the solubility measurements undertaken in this work, were performed in an acidic medium, using stoichiometric amounts of $Ni(OH)_2$ and H_2SO_4, where the initial pH of the acid solution in one series was diluted to provide pH 1.9 and in the second 2.8 The presented investigations were carried out with nickel hydroxide samples: freshly settled, stored over 1 and 2 months as well as 6.5 years.

Analytical methods

Nickel concentration in leachate was determined with the atomic absorption spectrometry method (AAS) at a wavelength λ = 232.0 nm. The method was experimentally evaluated to be of a confidence interval of two standard deviations (α = 0.95) for the midpoint of the calibration curve ±1.1% of the measured value 10 mg/dm^3 and ±2.3% for a maximum point of 20 mg/dm^3. The detectable level of nickel by this method was 0.025 mg/dm^3.

Wide angle X-ray diffraction scattering (WAXS) examination

To determine the crystallinity of particular nickel hydroxide samples, the investigations were performed by X-ray pattern evaluation, using horizontal diffractometer TUR M-62 mated with a computer control. The examinations were performed by the WAXS method with the CuKα radiation at a wavelength of 1.5418°A and nickel filtering. The following measurement parameters were used: tension 30 kV; anodic current 25 mA; angle range 2θ: 3°–60°; counting step (2θ): 0.04°; counting time: 6s; with remaining standard parameters. The identification was performed by a comparative method, using standard X-ray patterns and the computer program X-RAYAN.

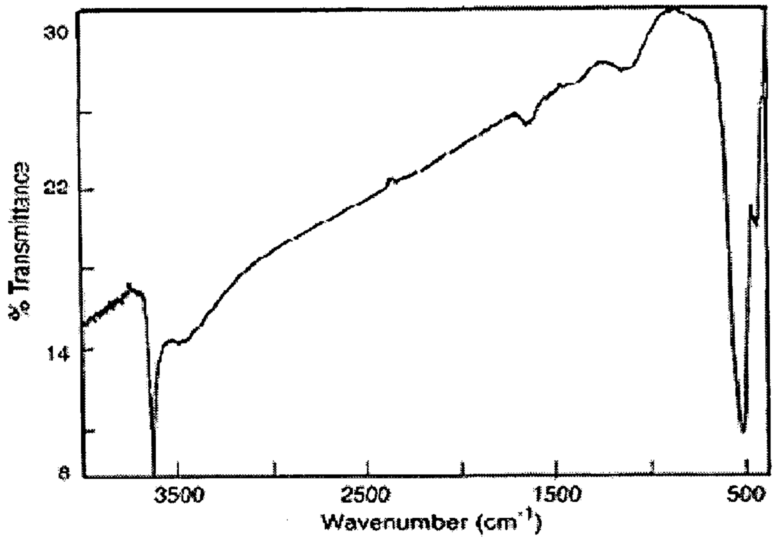


Fig.1.11 Infrared spectrum of the CA200 nickel hydroxide sample.(0 0 3) reflections (39° and 60.44° in 2*θ*).

The IR spectrum of the CA200 sample shown in Fig 1.11. is the one ideally expected for-$Ni(OH)_2$ .The crystallinity of the product is adversely affected on using a non-nitrate source. The PXRD pattern of nickel hydroxide obtained from nickel sulfate is given in Fig. and that for the product obtained from a reaction of NAS with a stoichiometric requirement of NaOH (final pH = 8.2) in Fig. This latter sample is X-ray amorphous. The IR spectrum is presented in Fig, and it exhibits all the features (T.N. Ramesh, P. Vishnu Kamath).

CHAPTER-2

LITERATURE REVIEW

T.N. Ramesh, P. Vishnu Kamath (2005) "Synthesis of nickel hydroxide: Effect of precipitation conditions on phase selectivity and structural disorder".

The synthesis of nickel hydroxide by precipitation from a suitable solution containing dissolved Ni^{2+} ions is described. A large matrix of precipitation conditions is explored to generate a wide range of nickel hydroxide samples. While most precipitation reactions result in the formation of-nickel hydroxide, the samples differ from one another in the degree of structural disorder as reflected by the differences in their powder X-ray diffraction (PXRD) patterns. A correlation of the long-range structure as deduced from diffraction studies with the short-range structure as deduced from infrared (IR) spectral studies is performed. The aim is to control the synthesis conditions to obtain materials with 'tailor-made' structural disorders.

Nickel hydroxide has a low solubility product ($1.6\times10{-}14$) and is therefore prepared by alkali-induced precipitation from a suitable nickel salt solution. Any change in the precipitation conditions affects the structure, composition and morphology of nickel hydroxide with a profound and often unpredictable impact on the reversible charge-storage capacity.

Strong alkali induced precipitation

Nickel hydroxide samples were precipitated by the addition of NaOH(2M) solution to a solution of nickel nitrate (1M) at ambient temperature (28–30°C) using a Metrohm Model 718 STAT Titrino operated in the pH-stat mode. Nickel hydroxide precipitation begins at pH = 5.5–6. In separate experiments, the alkali addition was stopped at final pH values of 7, 9 and 12, respectively, to study the effect of pH on the product. These samples were labeled 7SH, 9SH and 12SH (SH: sodium hydroxide), respectively.

Ammonia-induced precipitation

Ammonia-induced precipitation at low temperature (4°C), WH4, yields a poorly ordered nickel hydroxide, while at high temperature (25–65°C), $Ni(OH)_2$ is obtained with a surprisingly high degree of crystallinity . The PXRD pattern of WH4(Fig2.1) is characteristic of a material with turbostratic disorder .The two high-angle reflections are accordingly indexed to reflect the two-dimensional ordering of nickel hydroxide sheets. The low-angle reflection appearing at 7.6 °A corresponds to the inter-layer spacing in nickel hydroxide. The IR spectra also reflect the dramatic changes brought about by the change in temperature (.WH4 exhibits all the characteristic absorptions of nickel hydroxide, while WH25 shows the features of $Ni(OH)_2$.

When nickel hydroxide (WH4) is aged in concentrated ammonia at ambient temperature, it transforms into crystalline $Ni(OH)_2$ (see Fig2.1. for the PXRD pattern of a partially-transformed sample). On ageing in concentrated alkali (6M KOH), it transforms into β_{bc} nickel hydroxide (Fig.2.1). This clearly shows that the pH during ageing has a profound affect on structural disorder. Fig 2.1. PXRD pattern of (a) WH4 sample compared with that of (b) WH25 sample. **Note; WH- weak hydroxide**

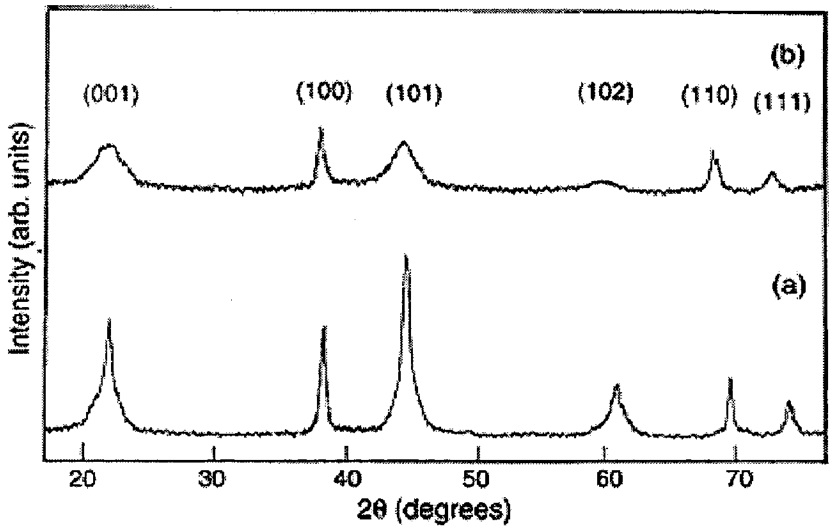
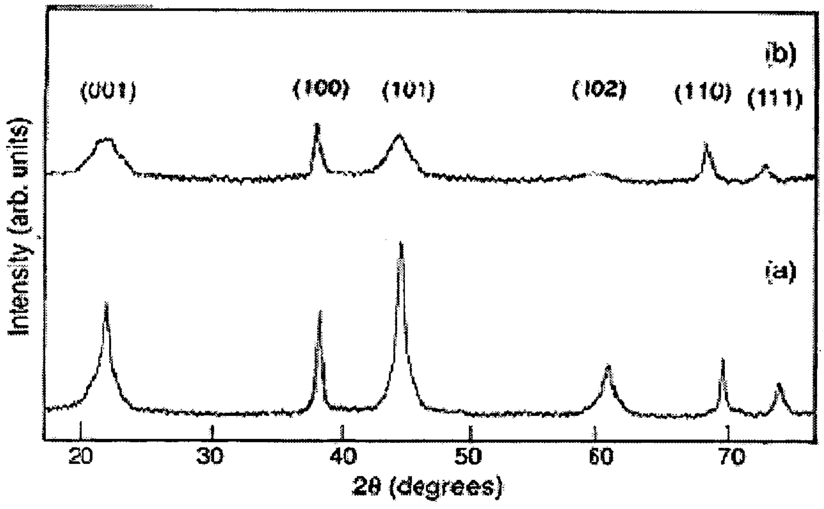


Fig.2.1 PXRD pattern of (a) WH4 sample compared with that of (b) WH25 sample Note; WH- weak hydroxide Disorder→Order transformation in nickel hydroxide system

Precipitation of a solid takes place when two solutions having different free energies are mixed. According to Ostwald's law, the solid obtained immediately on precipitation is not only disordered but also thermodynamically unstable with a free energy close to that of the reactants. The disordered phase transforms into a more stable phase of lower free energy in a step-wise manner. During the precipitation of nickel hydroxide, especially at low temperatures and moderate pH conditions as obtained during ammonia induced precipitations or stoichiometric strong alkali addition, the solid formed immediately on precipitation is the amorphous phase (Fig 2.2). This phase is metastable and transforms into other phases of progressively greater order and thermodynamic stability.



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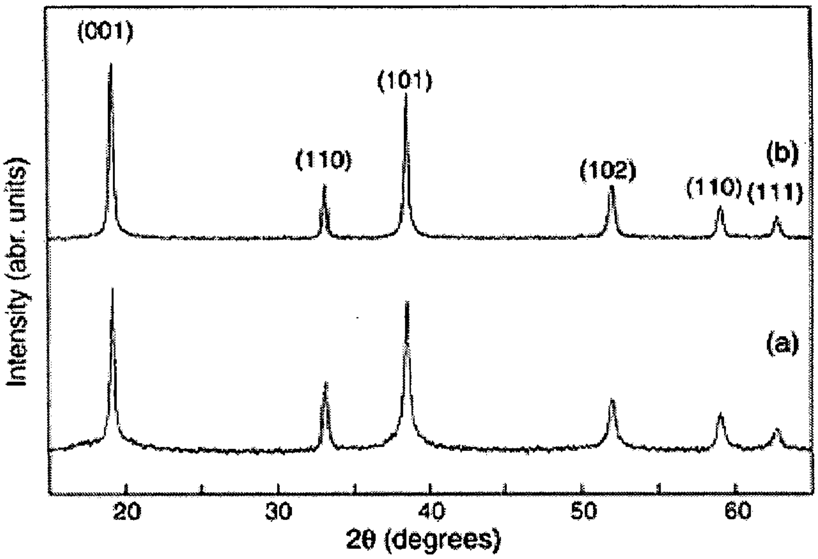

Fig.2.3 PXRD patterns for nickel hydroxide samples obtained by (a) removal of ammonia and (b) diffusion methods.

In the former method, ammonia has been introduced slowly with the object of forming the nickel ammine complex in site followed by hydrolysis. The latter method starts from the complex and facilitates precipitation by controlled decomposition of the complex by the slow removal of ammonia.

Cinziana Sist and George P. Demopoulos (2001)"Nickel Hydroxide Precipitation from Aqueous Sulfate Media"

In some of the process flow sheets, nickel hydroxide precipitation is incorporated. For these operations, the optimization of nickel hydroxide precipitation is important to assure efficiency and product quality. The main objective of this investigation was to study and improve the precipitation characteristics of $Ni(OH)_2$ in a sulfate system using supersaturation controlled precipitation. One possible technique used to produce a superior product is controlled supersaturation,11 which aids in generating well-grown crystalline particles. Precipitates formed via homogeneous nucleation typically possess undesirable properties such as bad morphology (i.e., amorphous or badly formed crystals), slow settling rates, low solids density, and high impurity uptake.

The solubility of nickel hydroxide as a function of pH at various temperatures is crucial to define the operating window in which to control precipitation (Fig 2.4). It is well known that the solubility of a compound is affected by the degree of crystallinity of the solid;

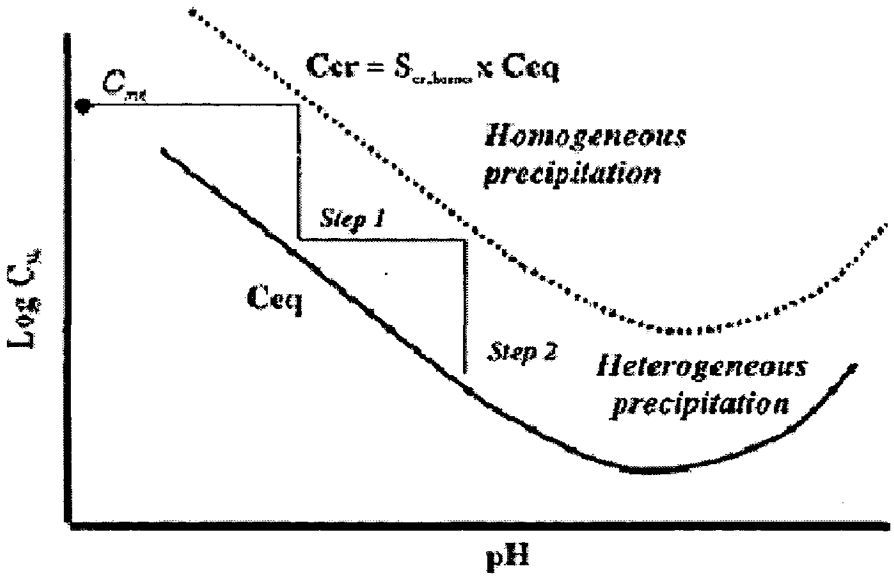

Fig. 2.4 controlled supersaturation technique for producing well-formed precipitates

Małgorzata Osinska , Tadeusz Stefanowicz, Dominik Paukszta (2004) " Journal of Hazardous Materials"

Nickel hydroxide samples freshly settled as well as stored over 1 month, 2 months and 6.5 years were examined for their solubility rate in diluted H_2SO_4 solutions of pH 1.9 and 2.8 as a function of time. Samples with a longer ageing history dissolved less readily than freshly settled ones. It was determined that the resistance to dissolving rose with sample ageing time and the solubility of the 6.5 years stored sample was particularly low. X-ray examination evidenced that during storage the crystallinity of $Ni(OH)_2$ subsequently rose. The parallelity of both time-dependent phenomena allows the conclusion that with nickel hydroxide ageing the transformation of disordered nickel hydroxide species into crystalline $Ni(OH)_2$ (without phase changes) is responsible for increasing nickel hydroxide resistance to dissolving in acidic solutions. Such decrease of nickel hydroxide solubility with ageing in case of waste nickel hydroxide, is worth to notice in a view of environment protection against pollution with electroplating waste.

Waste electroplating sludge due to high concentrations of heavy metals is highly dangerous to dispose of in landfills without careful protection against metals leaching into the ground. Usually, stabilization and solidification are considered as effective methods in such protection. Sometimes electroplating sludge, which contains mainly metal hydroxides, is utilized by admixing it to ceramic building materials. Such admixture to building wares is permitted in Poland (excluding buildings for human habitation) under the condition that the total concentration of heavy metals in water leachate obtained during 48 h stirring at a water-to-sample mass ratio 10:1 does not exceed 10 mg/dm^3. Having in mind the eventual ecological consequences of such electroplating waste sludge admixing to building materials, a number of metal leaching examinations were performed with ceramics which were prepared with admixtures of metal hydroxides, such as copper, chromium, iron and nickel hydroxides as well as with their mixtures. As the environmental pollution danger from such admixtures greatly depends on their leaching, the examination of particular metal hydroxides solubility is the important factor worth examining due to ecological views.

The metal hydroxide ageing time influence on its solubility and the eventual reasons of such influence are of particular interest. Recent investigations were conducted with nickel hydroxide precipitate. Its solubility in neutral water is highly dependent on a solution pH with a minimum value of pH 10, at which it falls to 10^{-3} mg/dm^3. In order to obtain more precise measurable nickel ion concentrations, the solubility measurements undertaken in this work, were performed in an acidic medium, using stoichiometric amounts of $Ni(OH)_2$ and H_2SO_4, where the initial pH of the acid solution in one series was diluted to provide pH 1.9 and in the second 2.8 The presented investigations were carried out with nickel hydroxide samples: freshly settled, stored over 1 and 2 months as well as 6.5 years.

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Nickel concentration in leachate was determined with the atomic absorption spectrometry method (AAS) at a wavelength λ = 232.0 nm. The method was experimentally evaluated to be of a confidence interval of two standard deviations (α = 0.95) for the midpoint of the calibration curve ±1.1% of the measured value 10 mg/dm^3 and ±2.3% for a maximum point of 20 mg/dm^3. The detectable level of nickel by this method was 0.025 mg/dm^3.

Wide angle X-ray diffraction scattering (WAXS) examination

To determine the crystallinity of particular nickel hydroxide samples, the investigations were performed by X-ray pattern evaluation, using horizontal diffractometer TUR M-62 mated with a computer control. The examinations were performed by the WAXS method with the CuKα radiation at a wavelength of 1.5418°A and nickel filtering. The following measurement parameters were used: tension 30 kV; anodic current 25 mA; angle range 2θ: 3°–60°; counting step (2θ): 0.04°; counting time: 6s; with remaining standard parameters. The identification was performed by a comparative method, using standard X-ray patterns and the computer program X-RAYAN.

X-ray examinations

The X-ray patterns of each sample are presented in Fig. 1. The examination of freshly settled and wet $Ni(OH)_2$ (sample a) evidenced that apart from an disordered $Ni(OH)_2$ form, already some hours following precipitation, the X-ray pattern facilitates the detection of diffraction maxima which originate from the crystalline structure of $Ni(OH)_2$. Especially distinct maxima appeared at the angles $2\theta = 33.0°$, 38.5° and 59.0°. After one month storage (at ambient temperature) the share of the crystalline $Ni(OH)_2$ phase increased as all said characteristic maxima of crystalline form of nickel hydroxide were shaped more distinctly and additional characteristic reflexes occurred at the angles 2θ: 19.3° and 52.0° (sample b). After 2 months storage in similar conditions the share of crystalline $Ni(OH)_2$ forms increased even more significantly (sample c), especially if compared with the X-ray pattern of sample a. The examination of sampled, stored wet over 3.3 years (40 months), revealed a further increase in distinctly shaped reflexes pertinent to crystalline form of $Ni(OH)_2$. It was evidenced that during ageing, water molecules housed between layered sheets of freshly settled $Ni(OH)_2$ leave the intersheet layer, resulting in more compact structure. This in turn implies the secondary consequences, such as increase of nickel hydroxide specific gravity and decrease of its specific surface. It should be emphasized however that particular X-ray patterns demonstrate the increasing crystallinity, while the polymorfic changes were not observed (phase remains the same, i.e. the theoprastite). To determine what influence such changes of crystallinity exert on nickel hydroxide leaching, the solubility trials with differently aged $Ni(OH)_2$ were undertaken.

For a more distinct differentiation of solubility results, the leaching trials were performed in water acidified with sulphuric acid in the first series to pH 1.9 and in the second one to pH 2.8. The nickel hydroxide dissolving course in diluted H_2SO_4 solution of pH 1.9 was displayed in percents of dissolved Ni^{2+} amount with respect to total nickel content introduced with nickel hydroxide precipitate (Fig2.5). In parallel the pH readouts of suspension during 300 min are shown in Fig 2.7. Similarly, the share (%) of dissolved Ni^{2+} in diluted H_2SO_4 solution of pH 2.8 was displayed in Fig 2.6 and changes of pH in

Fig.2.7. As follows from Fig.2.5, the freshly settled nickel hydroxide dissolved thoroughly in sulphuric acid solution of pH 1.9 after 50 min, the sample stored over one month, after 90 min and the sample stored over 2 months dissolved as much as approximately 81% after 180 min. The sample stored over 6.5 years dissolved as much as 27% after 180 min (and nearly thoroughly after 8 days). As follows from the pH changes (Fig 2.5), the dissolving speed was greatest during the first 20 min (excluding the 6.5-year-old sample, where pH change was permanently slow). The second series examination performed in a sulphuric acid solution of initial pH 2.8 displayed less steeply, however at the same sequence laid dissolving curves (Fig2.6). The freshly settled nickel hydroxide after 300 min dissolved as much as approximately 82%, the sample after 1 month storage- approximately 64% and the sample after 2 months storage— approximately 23%. The sample stored over 6.5 years after 300 min dissolved not more than 0.1(Malgorzata, Tadeusz, Dominik)

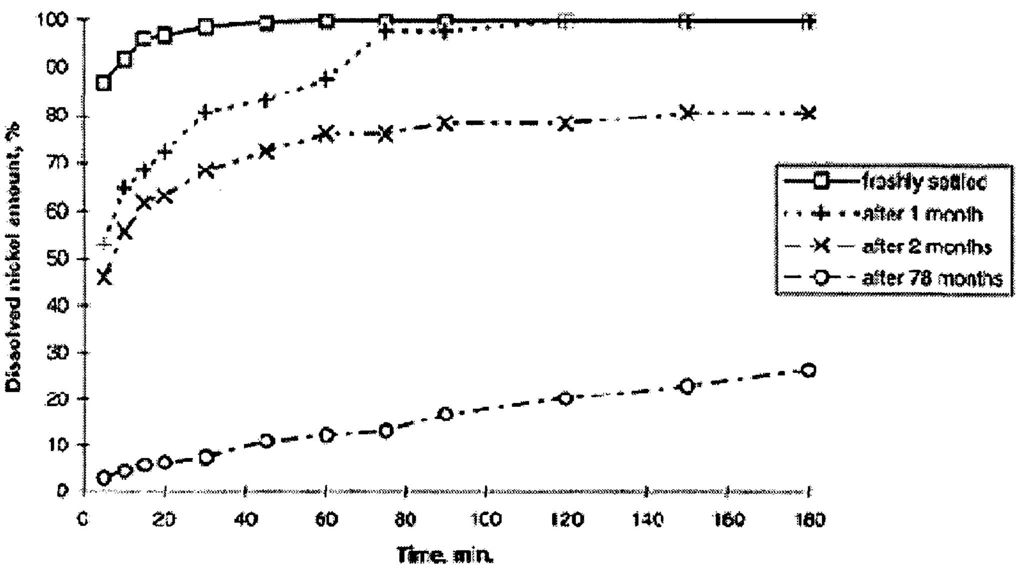


Fig. 2.5 The share of dissolved Ni^{2+} (%) in $Ni(OH)_2$ suspension in water acidified to pH 1.9 as a function of time for nickel hydroxide species: freshly settled, stored during 1, 2 and 78 months (6.5 years).

Changes of pH were also much slower and its value remained nearly at the same value for the sample stored over 6.5 years (Fig 2.7). It is natural to expect that depending on nickel hydroxide storage time (as a matter of fact—its crystallinity), its dissolving rate (at the constant temperature) is controlled by pH and by nickel ions concentration in surrounding solution, i.e. by its unsaturation level with respect to nickel hydroxide of particular development of crystallinity. The comparison of Figure above (as well as Figures given below) shows the mutual relation between the both said parameters, especially with respect to nickel hydroxide samples of the shorter age of storage. Nevertheless, considering said figures it is worth to notice that dissolving rate of the higher crystallinity 6.5 years aged $Ni(OH)_2$ sample is extremely low and pH influence seems to be significantly limited. It is logical to expect that decreased specific surface of aged nickel hydroxide additionally contributes to decreasing of its dissolving rate.

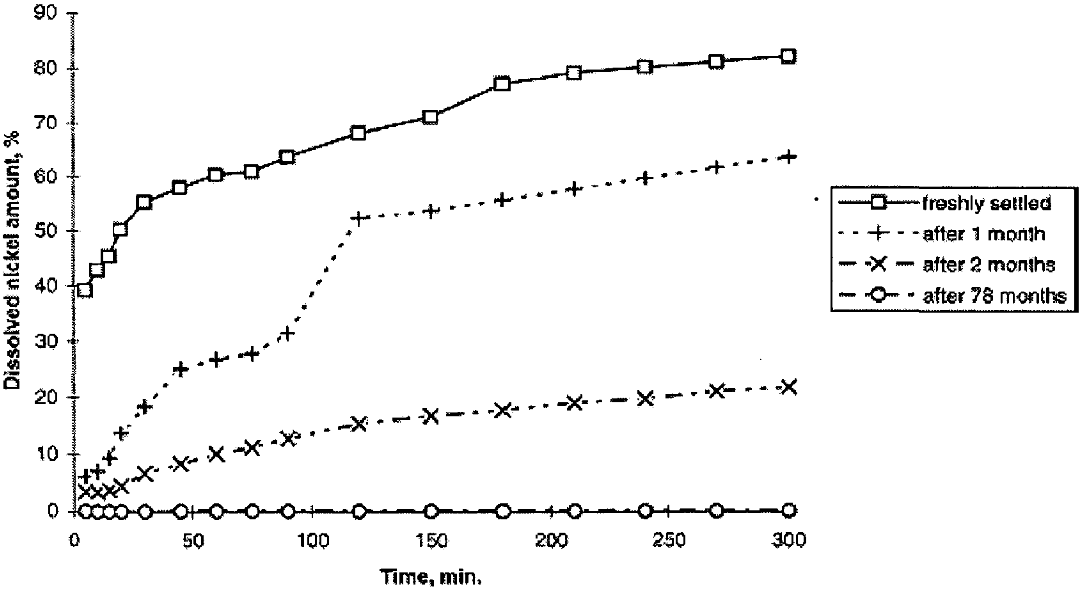


Fig.2.6 The share of dissolved Ni^{2+} (%) in $Ni(OH)_2$ suspension in water acidified to pH 2.8 as a function of time for nickel hydroxide species: freshly settled, stored during 1, 2 and 78 months (6.5 years).

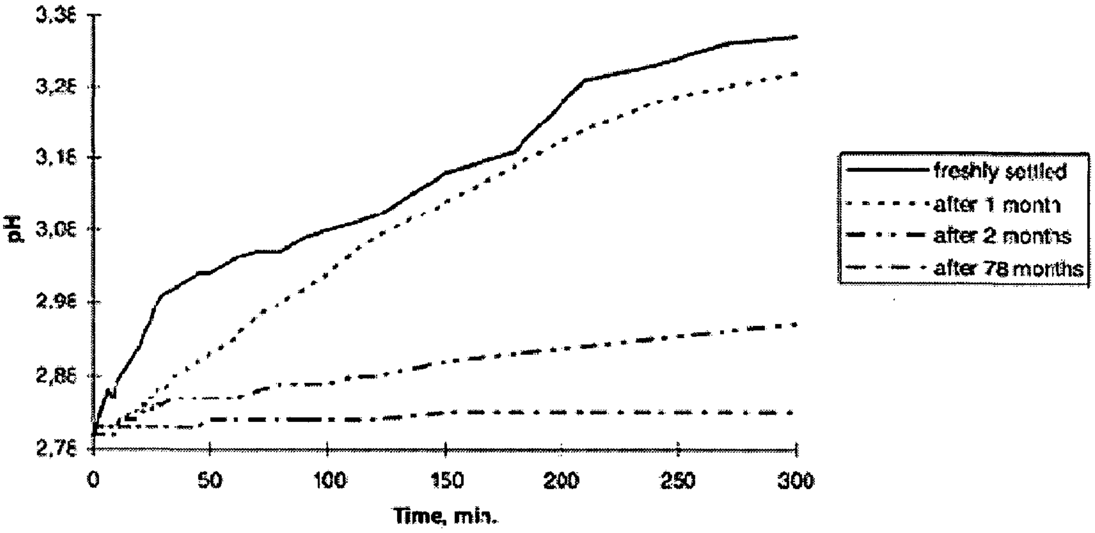


Fig.2.7 pH changes in $Ni(OH)_2$ suspension in water acidified to pH 2.8 as a function of time for nickel hydroxide species: freshly settled, stored during 1, 2 and 78 months (6.5 years).

However, the decrease in specific surface is only a secondary cause for reduction in the observed dissolution rate, while the main cause is the increase in $Ni(OH)_2$ crystallinity.

CHAPTER -3

3.1 PICKLING

Pickling is the process of treating steel with acid to remove scale and rust from the surface. Both of the conditions are harmful for subsequent forming or metal working operations. Scale because of its hardness can lead to reduction in die life, can increase slitter knives wear and affects rollability within gage tolerances. It may also increase the chances of decarburization in annealing operations. Rusty steel leads to a poor appearance in the final product not to mention the dirt accumulation in the equipment in contact with the steel.

When steel surfaces come in contact with the atmospheric oxygen at high temperature, higher oxides like Fe_2O_3, are formed which subsequently get reduced to lower oxides like Fe_3O_4 and FeO etc. nearer to the metal surface. This surface oxide film formed during the process of hot rolling consists mainly of FeO (85%) directly in contact with steel surface followed by thin layer of Fe_3O_4 (10-15%) at the middle and very fine film of Fe_2O_3 (0.5-2.0%) at the very top in contact with the atmosphere.

These composite films of scale need to be removed thoroughly to ensure good surface of the end product and better workability. This oxide layer is removed through the process of pickling in which the annealed sheets are washed and cleaned in the acidic solution containing inorganic acids taken in different proportions. Generally H_2SO_4 and HCI are used for the process but may vary with type of steel sheets to be pickled. Carbon steel is pickled with HCl, $H_2SO_4$and Stainless steel is pickled with HCl, HF and HNO_3 (Pickling handbook).

In the past pickling was done in batches. The steel was loaded in acid baths and then had to be loaded in other sections for rinsing and drying. With the high volume and tonnage requirements nowadays, continuous picklers where the entire operations with multiple acid tanks, rinsers, dryers and oilers are installed in series that can pickle around

60 tons/hour are common. Inspections in the pickle line are limited to gage, width and surface quality. Additional inspections may incur extra costs.

Steel fabrication processes often use pickling (immersing steel in acid) to remove oxide layers from recently heated steel. The Pickling process combines diffusion dialysis, energy transfer, and low temperature crystallization technologies to efficiently recover acids and metal salts. It has demonstrated significant gains in production capacity, quality control, and productivity by maintaining pickling tank acid and iron concentrations at preset levels. Bath uniformity and predictable performance raises output and minimizes rejects and rework. To manufacturers, these benefits are even more important than the simple cost savings from eliminating waste. Additional benefits include reduced demand for virgin acids and elimination of chemicals to neutralize waste acid, as well as energy and cost savings associated with acid transportation and disposal (K. Munns).

3.2 CHOICE OF METHOD

The choice of method and the extent of final cleaning required will depend on the need for corrosion resistance, hygienic considerations (pharmaceuticals, food) or whether visual appearance is the sole criterion. The routine removal of welding defects, welding oxides, organic substances and iron contaminants is normally a basic requirement and usually allows a comparatively free choice of final treatment. Provided that the surface roughness so permits, both mechanical and chemical methods can be used. However, if an entirely mechanical cleaning method is considered, the manufacturing stage has to be very well planned in order to avoid iron contamination, since decontamination, probably with nitric acid, will otherwise be necessary . When requirements as to surface finish and corrosion resistance are exacting, the choice of method is more critical. A treatment sequence based on pickling will in such cases provide the best chances of a superior result (Fig 3.1).

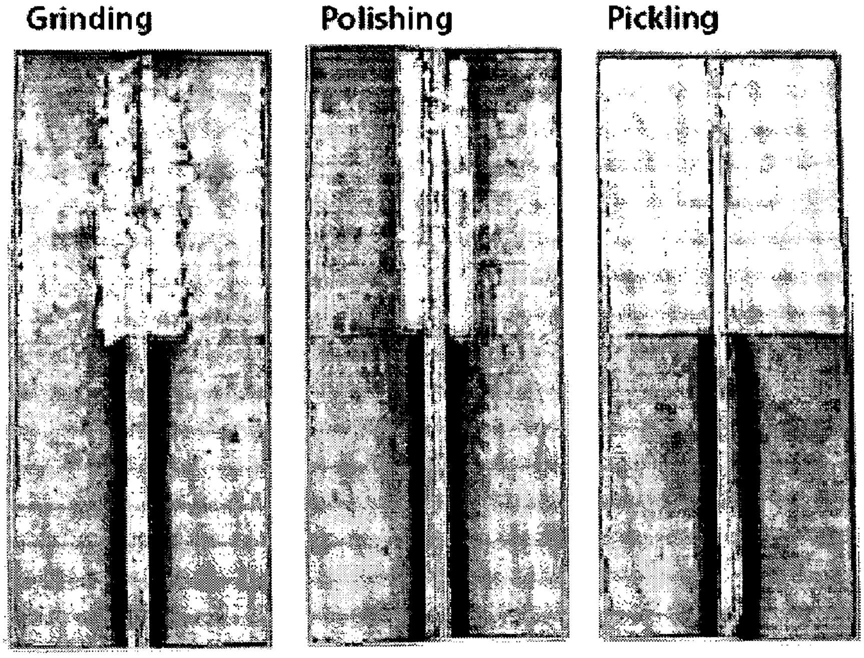


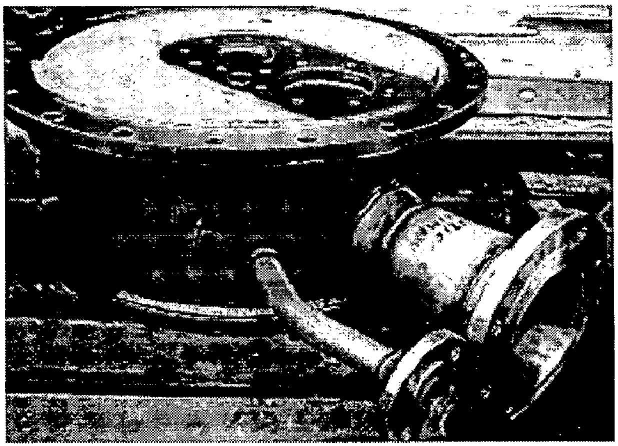
Fig.3.1 Pickling offers better results than alternative surface treatment such as grinding and polishing

Pickling products can be applied in three different ways

- Brushing, using a pickling paste/gel
- Spraying, using a pickling solution
- Immersion in a pickling bath

Heat tint on stainless steel fabrications can be removed using acidic brush-on pastes or gels, spray pickling, immersion tank pickling or electrochemical cleaning methods, following careful degreasing of the affected area (Fig 3.2). A combination of finishing techniques may be needed, as nitric acid treatments alone cannot be relied on to remove sufficient metal from the surface. This may include mechanical treatments (grinding or abrading) followed by nitric acid decontamination. It is important that heat tint is removed from hidden faces of welds on fabrications, where these faces are likely to be exposed to the service environment (Euro Inox)

Before pickling process;



After pickling process;

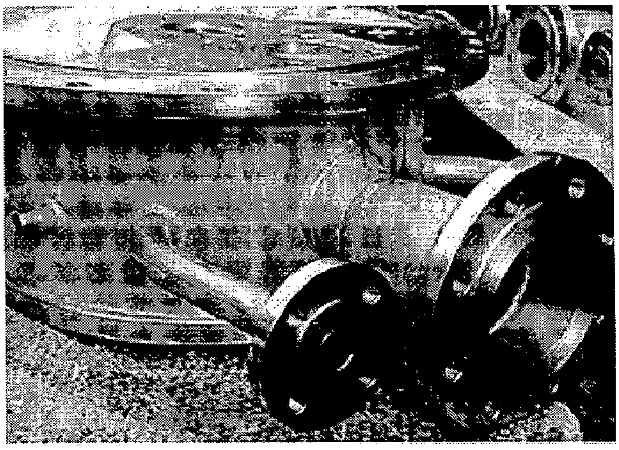


Fig. 3.2 Heat tint left in welded areas of a complex fabrication can be effectively removed by pickling by immersion pickling. The corrosion resistance of the whole fabrication has been restored by pickling.

3.3 SAFE HANDLING AND STORAGE OF PICKLING PRODUCTS

SAFETY RULES

Pickling products are hazardous substances that must be handled with care. A good, safe working environment requires the observance of certain rules:

1. The handling of pickling chemicals should be limited to persons with a fundamental knowledge of the health hazards associated with such chemicals. This means that the Material Safety Data Sheet and the product label should be thoroughly studied before the chemicals are used.
2. Eating, smoking and drinking should be forbidden in the pickling area.
3. Employees handling pickling chemicals should wash their hands and faces before eating and after finishing work.
4. An acid-resistant material such as polyethylene (PE), polypropylene (PP) or polyvinyl chloride (PVC) plastic should protect all parts of the skin that are exposed to splashing. This means that employees handling pickling chemicals (including during rinsing) should wear a facemask, rubber gloves, rubber boots and an overall.
5. Avesta First Aid Spray 910 should be readily available when handling Avesta Pickling Paste/ Gel/Spray for immediate treatment of smaller acid splashes on the skin or in the eyes. When handling larger volumes of acids, such as Avesta Pickling Bath,Hexafluorine in larger packages should be used. A physician should be consulted for subsequent treatment.
6. The pickling area should be ventilated.
7. To avoid unnecessary evaporation, the containers should be kept closed as much as possible.
8. In order to protect the environment, all pickling residues should be neutralized and the heavy metals present separated and sent to waste treatment plant (Pickling handbook).

PERSONAL SAFETY

Health hazards can be avoided by means of air protection and skin protection. We recommend that the following measures be adopted if a high degree of personal safety is to be assured. For personal safety, a facemask (equipped with breathing apparatus) should always be worn in connection with pickling operations. This mask should be equipped with a breathing filter, type B (grey) and a dust filter, type P2, all according to the Central European Norm (CEN). The pickling acids are aggressive and can cause burns by skin-contact. This can be avoided by protecting all exposed parts of the skin with acid resistant clothing. As a personal security measure, Avesta First Aid Spray 910 should be readily available at the workplace, in the event of acid splashes.

All pickling chemicals from AvestaPolarit Welding are provided with:

- Product Information (PI) with reference numbers; - Material Safety Data Sheets (MSDS) according to ISO 11000.

These documents give the information necessary for the safe handling of the product, and they should always be consulted before using the product. For further information, an Emergency Response Centre (ERC) could be contacted. They should have all the necessary information concerning AvestaPolarit Welding's pickling products and be able to give an immediate recommendation in the case of an accident (Pickling handbook)

3.4 STAINLESS STEEL PICKLING

The most common application for stainless steel pickling is "pickle/passivate". This is our "one-step" process which removes heat tint and weld scale while simultaneously passivating the surface of the parts being processed. Pickling also accomplishes passivation. However, pickle and passivate in two complete and separate steps.

The next most common application for stainless steel pickling is as a surface pre-treatment step prior to electropolishing. When a part has heat tint and weld scale recommends pickling prior to electropolishing to achieve the best results.

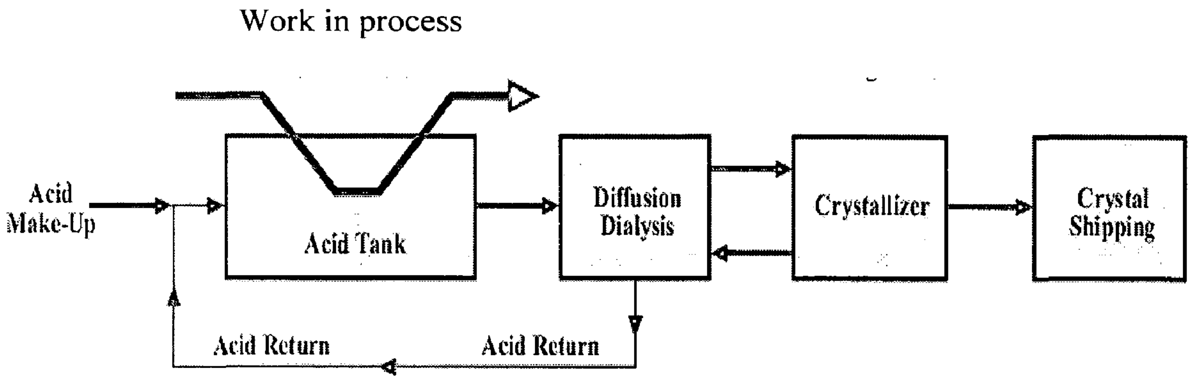


Fig 3.3 Recovery of Acids and Metal Salts from Pickling Liquors

Spent acid baths are produced in the pickling of stainless steel sheets. The aim of this operation is to remove the oxide scale layer formed over the steel sheets. It is carried out by submerging(1) the sheet in a HF-HNO_3 mixture.2-4 When metals concentration in solution reaches 5%, the acid bath has to be renewed.

The spent bath (known as spent pickling liquor, SPL) is composed by very stable iron and chromium fluoride complexes (as FeF_2^+, FeF^{2+}, and CrF_2^+ in solution),nickel (as Ni^{2+}), and free hydrofluoric and nitric acids (as HF, H^+, and NO_3^-), while metal-nitrate complexes, Fe^{3+} or Cr^{3+}, concentration is very low. Table shows the composition range of liquors coming from AISI304 steel pickling (Jorge Hermoso, Javier Dufour, Jose).

The weight loss and corrosion potential of oxidised and blank stainless steels pickled in HF are shown in Fig.3.4. The weight loss of oxidised stainless steel increases rapidly at the beginning due to the dissolution of metals and, as before, the undercut oxide scales (Fig.3.4). After about 70s, the increase in weight loss is significantly suppressed. On the other hand, a rather slight weight loss takes place on blank stainless steel throughout immersion in the electrolyte.

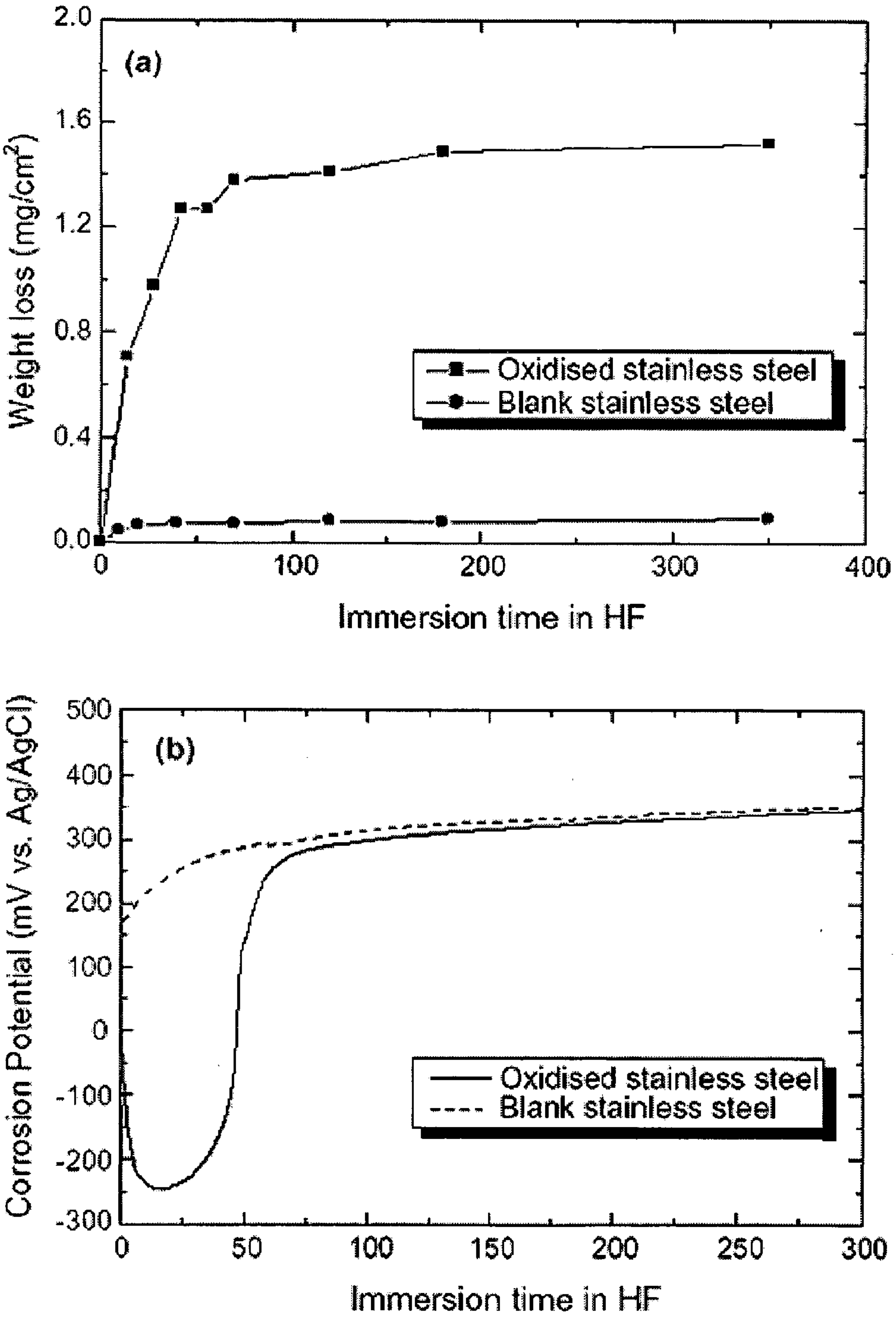


Fig. 3.4 Comparison of (a) weight loss and (b) corrosion potential of oxidized and blank stainless steels pickled in HF at 55 °C

3.5 CHEMICAL PROPERTIES OF PICKLING LIQOUR AND HYDROXIDE SLUDGE

The chemical properties of the stainless steel pickling liquor and hydroxide sludges have been investigated through chemical analysis, X-ray diffraction analysis, particle size distribution, scanning electron microscopy and thermal analysis. The reduction properties of the sludges have been studied through thermodynamic calculations and experimental reduction tests in laboratory scale. Drying properties have been investigated in a pilot scale drying equipment.

The agglomeration property has also been investigated. The sludges studied, have many common characteristics. The dry matter in the filter cakes is about 35-40 %. After drying at 120°C the sludges still contains 10-15 % water, as hydrates, which evaporates in the temperature range 120-600°C. The mean particle size is about 3.7 mm for both materials. The filter cakes are amorphous. When heated, several crystalline phases were identified. Scanning electron microscopy studies show that the elements Fe, Ni, Cr,F, Ca are evenly distributed between the particles. This implies that separation of CaF_2 by mechanical methods may be difficult. It was found that the agglomeration of these materials is difficult. After drying the strength increased, at higher temperatures the pellets started to decrepitate. In laboratory scale reduction tests the reduction degree of iron and nickel reached 94-98 % and 75-83 % respectively (Pickling handbook).

3.6 OBJECTIVES OF THESIS

On the basis of reviewed literature following objectives have been planned.

(i) To study the recovery of Nickel hydroxide from stainless steel pickling liquors.

(ii) To carryout the analyzing filter cake (precipitates).

CHAPTER 4

4.1 EXPERIMENTAL MECHANISM

The treatment of stainless steel pickling waste is compulsory due to its toxicity and polluting character. Moreover, metals and acids recovery is interesting from an economical point of view. SPL classical disposal consists of high-pH neutralization with lime and potassium or sodium hydroxide. This process generates high wastes volume and valuable materials lost, so recovery processes have been developed (Table 4.1). Free acid recovery processes do not regenerate HF or HNO_3 from metallic complexes in solution. However, acid retardation is the most implanted technique due to its low cost, although wastes volume is still high.

Total acid recovery processes try to recover the whole anions content in solution as acids. Extraction and evaporation have been implemented in steelmaking plants, while electrohydrolysis has been developed only on the pilot plant scale. Although SPL treatment processes literature refers to metals as byproducts, iron chromium and nickel are usually precipitated with alkali, obtaining high-fluoride containing solid, which is not recyclable and has to be disposed off as a toxic waste. Pyrohydrolysis13 consists of SPL spray roasting. Products of this reaction are nitric and hydrofluoric acid vapors and metal oxides obtained as pellets.

This technique achieves great yields for hydrofluoric acid, but the installation costs are high. The process proposed in the Chemical Engineering Department of the Complutense University of Madrid is designed for acid and metals recovery.

Figure shows a scheme of this process, which consists of several stages:

1. Selective precipitation of iron and chromium as fluorides, keeping nickel in solution.
2. Hydrolysis of iron and chromium solid fluorides by reaction with concentrated potassium hydroxide, releasing potassium fluoride to solution and recovering iron
3. and chromium as hydroxides.

4. Nickel hydroxide precipitation, by adding KOH to the liquid effluent from selective precipitation of iron and chromium.
5. Acid recovery, treating final effluents from $Ni(OH)_2$ precipitation and fluorides hydrolysis by means of ion exchange columns. Another studied possibility is the
6. utilization of bipolar membrane electrodialysis in order to recover and concentrate nitric and hydrofluoric acids.

The expected reaction mechanism is presented in Figure. The main reactions are those providing the desired products: intermediate fluorides (selective precipitation, Fig 4.1 , stage 1) and hydroxides of iron and chromium (hydrolysis, Fig 4.1 , stage 2), and nickel (Fig 4.1, stage 3)(Jorge Hermoso, Javier Dufour,Carlos Negro)

Table 4.1 SPL Industrial Treatment Processes

Material recovered	**Commercial processes**	**Technique**	**Industrial plant**	**Yield**		
				HNO_3	**HF**	**Metals**
Free acid	RECOFLO	Acid retardation	Simple	95%	80%	No
	TOKUYAMA SODA	Diffusion dialysis	Simple	96%	50%	No
Free+Complex acid	KAWASAKI	Extraction	Complex	97%	70%	Partial
	FLUOREX	Evap/acid ret.	Complex	99%	94%	No
	OPAR	Evaporation	Complex	99%	96%	No
	AQUATECH	Electro Hydrolysis	Complex	99%	93%	No
Acid +Metals	PYROMARS	Pyrohydrolysis	High Complexity	90%	97%	Potential

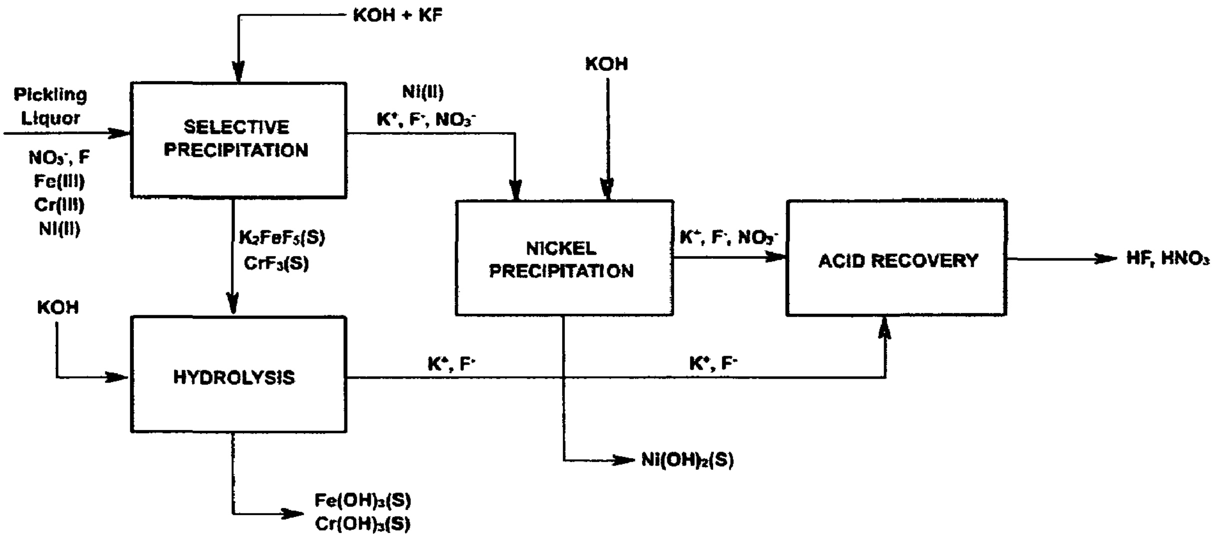


Fig.4.1 Block diagram of the process for overall recovery of stainless steel pickling liquors

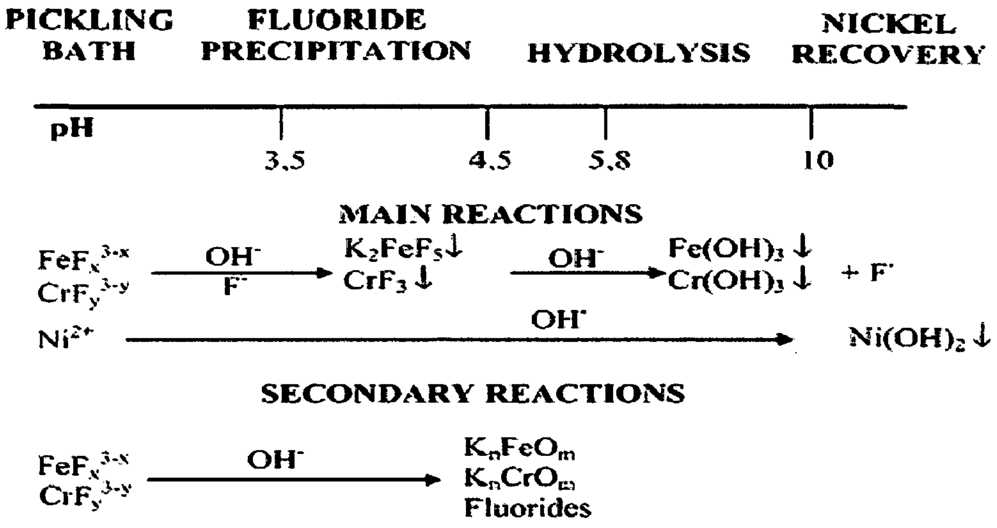


Fig.4.2 Expected reaction mechanism for SPL.

4.2 EXPERIMENTAL SETUP

A synthetic pickling liquor was prepared by dissolving16 stainless steel sheets in a mixture of nitric and hydrofluoric acids. The produced liquors are in the concentration ranges summarized in Table(4.2)

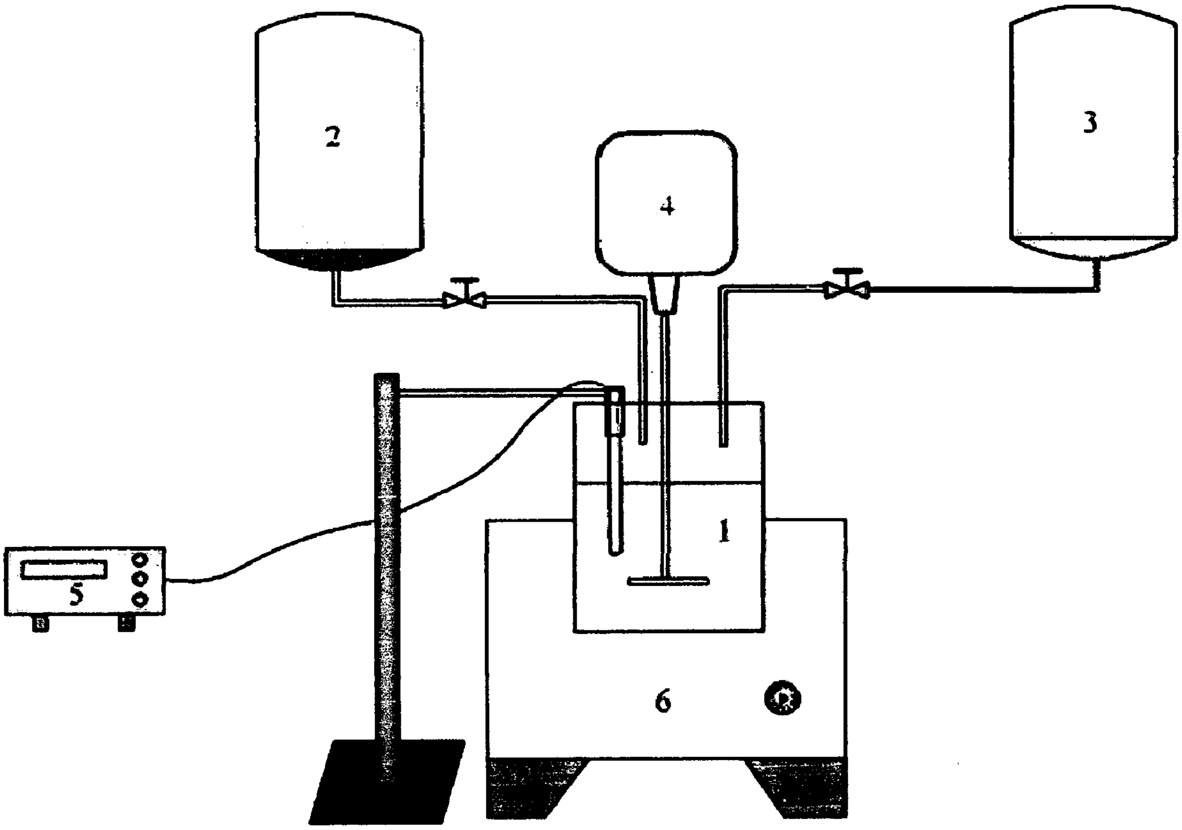


Fig.4.3 Experimental installation.

1.Cylinderical stirred glass reactor (CMSMPR)
2.Pickling liquor vessel (1lit)
3.KOH vessel
4. Electrical stirrer
5.pH meter
6.Thermostatic bath

The installation used to carry out the experimentation is shown in Fig 4.3. It consisted of a 2 L cylindrical stirred glass reactor (1) that worked as a CMSMPR one (Continuous Mixed Solid Mixed Product Removal). At the beginning of each experiment, 700 ml of water was introduced in the reactor to avoid conditions of massive precipitation. The pickling liquor and the alkali (potassium hydroxide 1.5 M, *Panreac-*

reagent grade) were fed from 2 L deposits (2,3), the liquor with a constant flow of 7 ml/min, while alkali flow was fed up to when operation pH is reached. A pH electrode kept in to the reactor and it connected to the pH meter. Temperature was maintained constant by submerging the reaction vessel in a thermostatic bath (6). Stirring speed was 200 rpm. The stationary state was reached after 2-2.5 h of reaction, depending on the experimental conditions. Samples of effluent were taken every 30 min for 3 h.

4.3 EXPERIMENT FOR PICKLING LIQUOR PREPARATION

Austenitic grade ;(AISI 304 Stainless Steel)

Cr(17-19%),Ni(8-11%),C(0.05%)

Pickling liquor preparation;

In industries following ratio of acid bath is prepare for tonnes of stainless steel pickling process;

52% nitric acid (36 ° Baume) : 100 lit
65 % hydrofluoric acid : 20 lit
or sodium fluoride : 30 kg
water : 900 lit

In experimetal work;

40 % hydrofluoric acid : 66 ml
52 % nitric acid : 168 ml
Distilled water : 766 ml

Experimental procedure;

Dip the staniless steel plate in the acid bath having the concentration mentioned above.After 2-3 hr remove it and the solution obtained is pickling liquor with the metal and the acid(HF,HNO_3).The concentration of the metal and the acids are obtained by the pickling process is given in the Table4.1 & 4.2 for the experiment 1&2, 3.

Time required for pickling process;

At 20°C 15min -3hr,at low temperature60-90min.

Stainless steel plates dimensions;

Length of plate = 8cm

Width = 4cm.

Area of one plate = 8×4 cm^2

No of plates = 57

KOH solution (1.5M);

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Lit of solution}}$$

Molecular weight of potassium hydroxide = 56.09

Weight of potassium hydroxide taken = 84.135

1.5 M KOH solution = 84.135 gm potassium hydroxide in 1 lit distilled water.

KF solution;

5% KF solution = 5% of KOH

= $(5/100) \times 84.135$

= 4.2068 gm KF

7.5% KF solution = 7.5% of KOH

= (7.5/100) × 84.135

= 6.3101 gm KF

10 % KF solution = 10 % of KOH

= (10/100) × 84.135

= 8.4135 gm KF

15 % KF solution = 15 % of KOH

= (15/100) × 84.135

= 12.6203 gm KF

Table 4.2. Mean Composition of Nitric-Hydrofluoric Spent Pickling Baths

1st & 2nd Experiment;

Compound	Concentration (g/l)
HNO_3	128-159
HF	16-28
Total nitrate	154-185
Total fluoride	56-78
Fe	30.13
Cr	7.31
Ni	5.75

3rd Experiment;

Compound	Concentration (g/l)
HNO_3	130-160
HF	18-28
Total nitrate	156-186
Total fluoride	60-80
Fe	31.88
Cr	8.37
Ni	6.44

4.4 EXPERIMENTAL PROCEDURE;

NICKEL HYDROXIDE PRECIPITATION

1. Initially 700 ml of water was introduced in the 2 lit cylindrical glass stirred reactor.
2. Pickling liquor is fed in to the reactor with constant flow rate (7ml/min).
3. Temperature was maintained as constant.
4. 1.5 M Alkali solution (KOH panreac grade +X% of KF) was fed to the glass reactor.
5. Stirring speed was maintained 200 rpm.
6. This condition was maintained for 2-2.5 hr.
7. After 2-2.5 hr stationary state was reached .
8. Samples were taken every 30 min for 3 hr.

Experiment 2;

Sample	Temp (°C)	pH	%KF	Fe (g/l)	Cr (g/l)	Fe + Cr (g/l)	K (g/l)	Ni (g/l)	Ni recovery %
1	45.0	3.77	7.5	2.5473	1.1790	3.7263	19.15	1.2862	77.62
2	47.0	3.80	7.5	2.6970	1.1832	3.8802	18.80	1.3304	76.86
3	49.0	3.90	7.5	1.7493	1.1102	2.8595	28.40	1.3772	76.05
4	50.0	4.00	7.5	1.9678	1.2130	3.1808	25.75	1.3952	75.74
5	52.5	3.75	7.5	2.5870	1.5278	4.1148	28.45	1.6056	72.08
6	52.5	3.90	7.5	2.4280	1.2516	3.6796	22.35	1.7100	70.26
7	52.5	4.10	7.5	1.5922	1.1124	2.7046	24.35	1.7206	70.08
8	52.5	4.25	7.5	1.8370	1.0274	2.8644	21.85	1.6974	70.48
9	52.5	4.50	7.5	0.9480	0.8298	1.7778	24.80	1.7548	69.48
10	55.0	4.20	7.5	1.4653	1.0040	2.4693	19.95	1.8444	67.93
11	55.0	4.40	7.5	1.1880	0.8480	2.0360	20.55	1.7617	69.36
12	60.0	4.30	7.5	0.7558	0.6346	1.3904	21.00	1.7308	69.89
13	65.0	3.80	7.5	1.6863	1.0672	2.7535	24.55	2.0056	64.42
14	65.0	4.00	7.5	1.6206	0.9574	2.5780	44.90	1.9226	66.56
15	65.0	4.50	7.5	0.4810	0.4500	0.9310	32.40	2.0980	63.51

7.5% KF solution = 7.5% of KOH

= (7.5/100) × 84.135

= 6.3101 gm KF

10 % KF solution = 10 % of KOH

= (10/100) × 84.135

= 8.4135 gm KF

15 % KF solution = 15 % of KOH

= (15/100) × 84.135

= 12.6203 gm KF

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1st & 2nd Experiment;

Compound	**Concentration (g/l)**
HNO_3	128-159
HF	16-28
Total nitrate	154-185
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Cr	7.31
Ni	5.75

3rd Experiment;

Compound	Concentration (g/l)
HNO_3	130-160
HF	18-28
Total nitrate	156-186
Total fluoride	60-80
Fe	31.88
Cr	8.37
Ni	6.44

4.4 EXPERIMENTAL PROCEDURE;

NICKEL HYDROXIDE PRECIPITATION

1. Initially 700 ml of water was introduced in the 2 lit cylindrical glass stirred reactor.
2. Pickling liquor is fed in to the reactor with constant flow rate (7ml/min).
3. Temperature was maintained as constant.
4. 1.5 M Alkali solution (KOH panreac grade +X% of KF) was fed to the glass reactor.
5. Stirring speed was maintained 200 rpm.
6. This condition was maintained for 2-2.5 hr.
7. After 2-2.5 hr stationary state was reached .
8. Samples were taken every 30 min for 3 hr.

9. The samples were filtered.
10. Filter cake was dried for 24 hr at 105 °C
11. Filtrate was diluted with Millipore water and analyzed for chromium,Nickel,Iron by Atomic Absorption Spectrophotometer (AAS).
12. Dried filter cake was milled and analyzed by X-Ray Diffractometer(XRD).

Table 4.2 Experimental results

Experiment 1;

Sample	Temp (°C)	pH	%KF	Fe (g/l)	Cr (g/l)	Fe + Cr (g/l)	K (g/l)	Ni (g/l)	Ni recovery %
1	40	3.10	5	0.4183	0.3183	0.7366	68.232	0.5119	91.07
2	40	3.35	5	0.2528	0.2696	0.5224	67.255	0.9653	83.21
3	40	3.50	5	0.0937	0.2520	0.3457	63.688	1.1792	79.49
4	40	3.70	5	0.1674	0.3201	0.4875	72.602	0.8054	85.99
5	45	3.90	5	0.4240	0.0000	0.4240	87.373	0.6401	88.86
6	45	4.10	5	0.0898	0.1985	0.2883	50.542	0.8108	85.90
7	45	4.29	5	0.0418	0.0618	0.1036	142.85	0.9586	83.33
8	45	4.20	5	0.0809	0.1311	0.2120	38.000	0.9926	82.73
9	45	4.50	5	0.0386	0.0461	0.0847	29.090	0.9497	83.48
10	45	4.40	5	0.0323	0.0586	0.0909	57.485	1.3686	76.19

Experiment 2;

Sample	Temp (°C)	pH	%KF	Fe (g/l)	Cr (g/l)	Fe + Cr (g/l)	K (g/l)	Ni (g/l)	Ni recovery %
1	45.0	3.77	7.5	2.5473	1.1790	3.7263	19.15	1.2862	77.62
2	47.0	3.80	7.5	2.6970	1.1832	3.8802	18.80	1.3304	76.86
3	49.0	3.90	7.5	1.7493	1.1102	2.8595	28.40	1.3772	76.05
4	50.0	4.00	7.5	1.9678	1.2130	3.1808	25.75	1.3952	75.74
5	52.5	3.75	7.5	2.5870	1.5278	4.1148	28.45	1.6056	72.08
6	52.5	3.90	7.5	2.4280	1.2516	3.6796	22.35	1.7100	70.26
7	52.5	4.10	7.5	1.5922	1.1124	2.7046	24.35	1.7206	70.08
8	52.5	4.25	7.5	1.8370	1.0274	2.8644	21.85	1.6974	70.48
9	52.5	4.50	7.5	0.9480	0.8298	1.7778	24.80	1.7548	69.48
10	55.0	4.20	7.5	1.4653	1.0040	2.4693	19.95	1.8444	67.93
11	55.0	4.40	7.5	1.1880	0.8480	2.0360	20.55	1.7617	69.36
12	60.0	4.30	7.5	0.7558	0.6346	1.3904	21.00	1.7308	69.89
13	65.0	3.80	7.5	1.6863	1.0672	2.7535	24.55	2.0056	64.42
14	65.0	4.00	7.5	1.6206	0.9574	2.5780	44.90	1.9226	66.56
15	65.0	4.50	7.5	0.4810	0.4500	0.9310	32.40	2.0980	63.51

Experiment 3;

Samples	Temp (°C)	pH	%KF	Fe (g/l)	Cr (g/l)	Fe + Cr (g/l)	K (g/l)	Ni (g/l)	Ni recovery %
1	50.0	3.80	10	3.9330	3.7225	7.6555	22.00	1.0800	83.22
2	51.0	3.90	10	1.3468	0.7895	2.1363	24.30	1.0867	83.12
3	52.5	4.00	10	0.9713	0.6245	1.5958	35.05	1.1065	82.81
4	52.5	4.00	10	0.8720	0.6963	1.5683	40.80	1.1935	81.46
5	53.0	4.01	10	0.6615	0.3705	1.0320	36.80	1.3270	79.38
6	55.0	4.03	10	1.1215	0.6395	1.7610	28.95	1.4125	78.06
7	52.5	4.05	10	0.6528	0.3908	1.0436	20.60	1.4142	78.03
8	52.5	4.07	10	0.6098	0.4008	1.0106	36.50	1.4130	78.05
9	52.5	4.10	10	0.5725	0.1785	0.7510	28.75	1.4457	77.54
10	52.5	4.15	10	0.2120	0.0390	0.2510	14.85	1.4797	77.01
11	50.0	3.97	15	0.3965	0.2093	0.6058	15.00	1.6103	74.98
12	40.0	3.61	15	1.3560	0.5328	1.8888	17.00	1.7445	72.89
13	40.0	4.00	15	0.7870	0.4790	1.2660	14.65	1.7440	72.91
14	40.0	4.25	15	0.1490	0.0430	0.1920	19.35	1.7540	72.75
15	40.0	4.50	15	0.0260	0.0203	0.0463	17.60	1.6292	74.69
16	45.0	4.00	15	0.6200	0.4053	1.0253	26.10	1.992	69.05

The samples were filtrated. The solid was dried for 24 h at 105 °C, milled, and analyzed by X-ray diffraction (XRD) using a Siemens Kristalloflex 810 goniometer with Fe & Cu KR radiation. Iron, chromium, nickel, and potassium concentrations in effluents and influents were analyzed with a Varian Spectra 220 atomic absorption spectrophotometer.

Nitrate and fluoride anions were measured with ion-selective electrodes (Mettler Toledo). Free acids concentration was determined by double titration with a Crison Compact D++ titrator.

4.5 Free acid concentration measurement;

1 ml of pickling liquor is neutralized with 1 M NaOH; equivalence point at pH 3.5-4.5 is considered to calculate total acidity. Simultaneously, 45 ml of pickling liquor reacts with 3 g of SiO_2, removing HF from solution. Titration of this HF-free solution led to HNO_3 concentration, while free hydrofluoric acid is assumed to be the difference between total acidity and nitric acid concentration.

Total acid concentration

1st titration;

pH of distilled water = 6.8

pH of pickling liquor = 1.75

pH of mixed liquor(1ml pickling liquor +distilled water) = 3.27

4.2 ml of 1M NaOH solution required for 1ml pickling liquor+99 ml distilled water to reach pH 5.52

2nd titration;

pH of distilled water = 6.8

pH of pickling liquor = 1.76

pH of mixed liquor(1ml pickling liquor + distilled water) = 3.26

4.2 ml of 1 M NaOH solution required for 1 ml pickling liquor + 99 ml distilled water to reach pH 5.52.

Nitric acid concentration

Adding 45 ml pickling liquor with 3 gm SiO_2 to remove HF acid from the solution.

1st titration;

45ml pickling liquor + 3 gm SiO2 solution pH =1.43

45ml pickling liquor + 3 gm SiO2 solution + 1M NaOH pH = 4.00

136 ml of 1 M NaOH required for 45 ml pickling liquor +3 gm SiO2 to reach the pH 4.0

2nd titration;

45ml pickling liquor + 3 gm SiO2 solution pH =1.43

45ml pickling liquor + 3 gm SiO2 solution + 1M NaOH pH = 4.00

135 ml of 1 M NaOH required for 45 ml pickling liquor +3 gm SiO2 to reach the pH 4.0

Calculation;

Total acid concentration

Molecular weight of NaOH = 39.998

1 ml pickling liquor requires 4.2 ml (1M) NaOH solution

Pickling liquor total acid concentration = 4.2 × 39.998 =167.9916 g/l

HF acid concentration;

45 ml pickling liquor required 135.5 ml of (1 M)NaOH solution

1 ml pickling liquor required = (135.5/45) =3.011 ml NaOH solution

HF acid concentration = $(4.2-3.011)\times 39.998 = 47.553$ g/l

Nitric acid concentration;

Total acid concentration = 167.9916 g/l

HF acid concentration = 47.553 g/l

HNO_3 acid concentration = $(167.9916 - 47.553) = 120.438$ g/l

CHPTER 5

5.1 RESULTS AND DISCUSSION

A factorial design was carried out to optimize nickel separation in selective precipitation. Previous works had shown that the influential variables in this stage were pH, temperature, and KF percentage in the alkali solution. The chosen experimental intervals were pH (3.5-4.5), temperature (40-65°C), and %KF (5-15%).

Analyzed responses were iron and chromium concentrations in the final effluent (separately), the sum of both concentrations in the final effluent, and nickel recovery percentage in solution. All those responses were studied at stationary state. The sum of the concentrations of iron and chromium was selected to optimize the purity of the nickel recovered in solution. The lower the sum was, the higher the purity was. Nickel purity was referred to the total metal concentration in solution.

On the other hand, nickel recovery response was defined as in eq 1

Equation 1

$$\textbf{Ni recovery} = \frac{F_{\text{Ni out}}}{F_{\text{Ni in}}} \times 100$$

where $F_{\text{Ni in}}$ and $F_{\text{Ni out}}$ were the steady-state mass flow of nickel entering and exiting the reaction vessel(g/l), respectively.

5.2 NICKEL RECOVERY IN THE FINAL EFFLUENT

A significant crossed interaction between temperature and %KF on nickel recovery can be observed in Fig5.7.& Fig 5.10 An increase of %KF at low-temperature conditions provoked a rising percentage of nickel recovery. The contrary effect occurred at high-temperature conditions. Thus, nickel recovery decreased when operation conditions were as follows: high temperature and high %KF in alkali.

Nickel did not take part in the reaction mechanisms for the studied pH range (3.5 - 4.5); it precipitated at pH higher than 9. Therefore, in the studied interval of variables, nickel was only removed from solution by coprecipitation with the complex iron and chromium fluorides, being promoted by high %KF and temperature that were the most favorable conditions to obtain the maximum nickel purity.

The final objective was to maximize nickel recovery with 100% purity. With this aim, the values of the variables that led to Fe + Cr = 0 . The results of the optimization are shown in Fig 5.1 to Fig 5.11. The non-continuous segments represent %KF values over 15, which were out of the experimental range. The optimum conditions that provided the maximum nickel recovery (74.69%) were as follows: T = 40°C, pH = 4.5, and 15% KF. The influence of pH could be observed: an increase of pH led to higher nickel recovery, but over pH 4.4 -4.7, a continuous decrease occurred, emphasizing the apparition of other precipitation mechanisms (metal hydroxides formation), which led to nickel removal by co-precipitation.

Experiment 1;

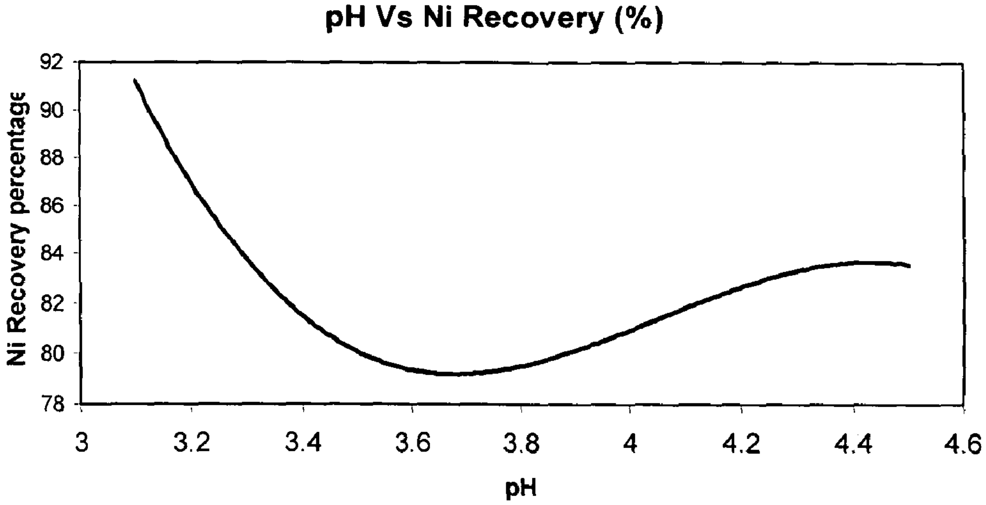


Fig 5.1 pH Vs Nickel recovery(%)

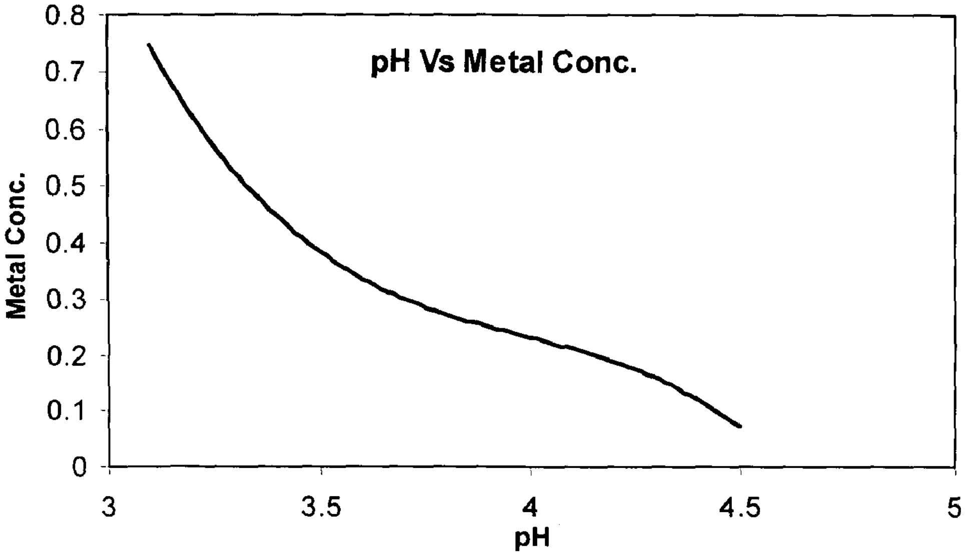


Fig 5.2 pH Vs Metal concentration

Experiment 2 ;

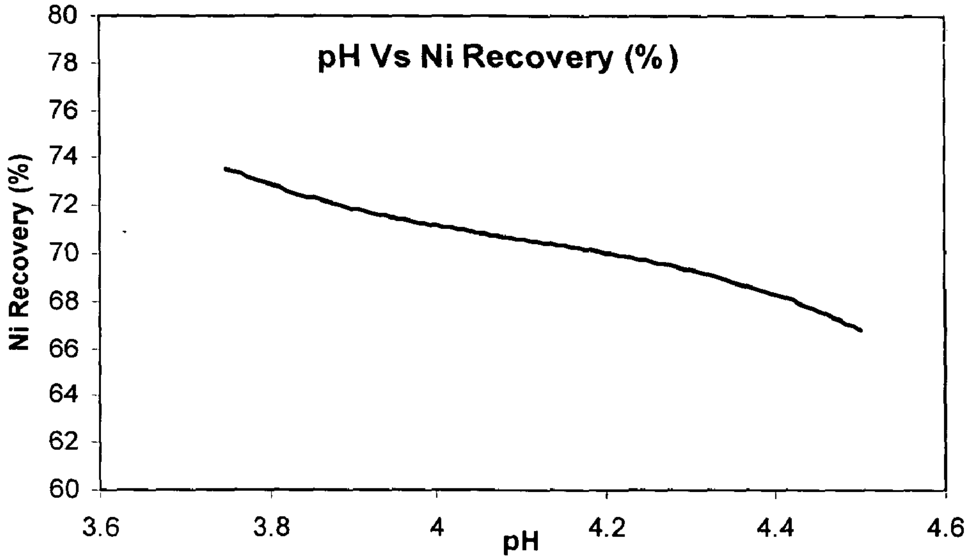


Fig 5.3 pH Vs Nickel Recovery (%)

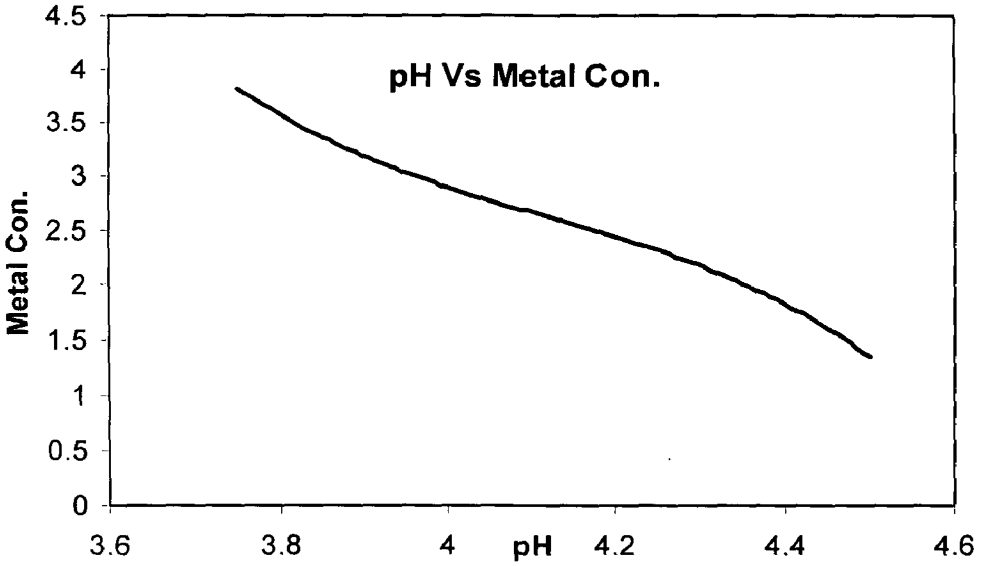


Fig 5.4 pH Vs Metals concentration

Experiment 3;

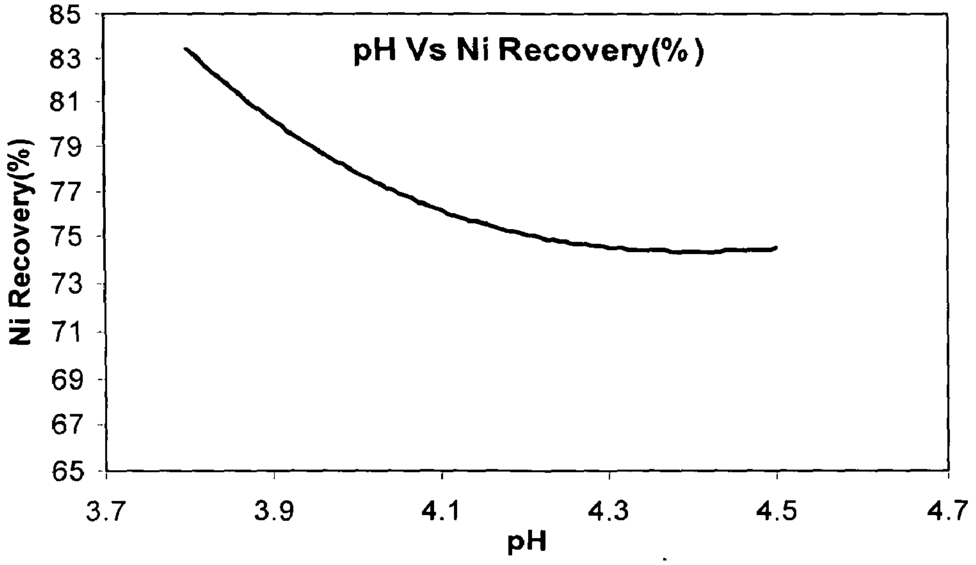


Fig 5.5 pH Vs Ni recovery(%)

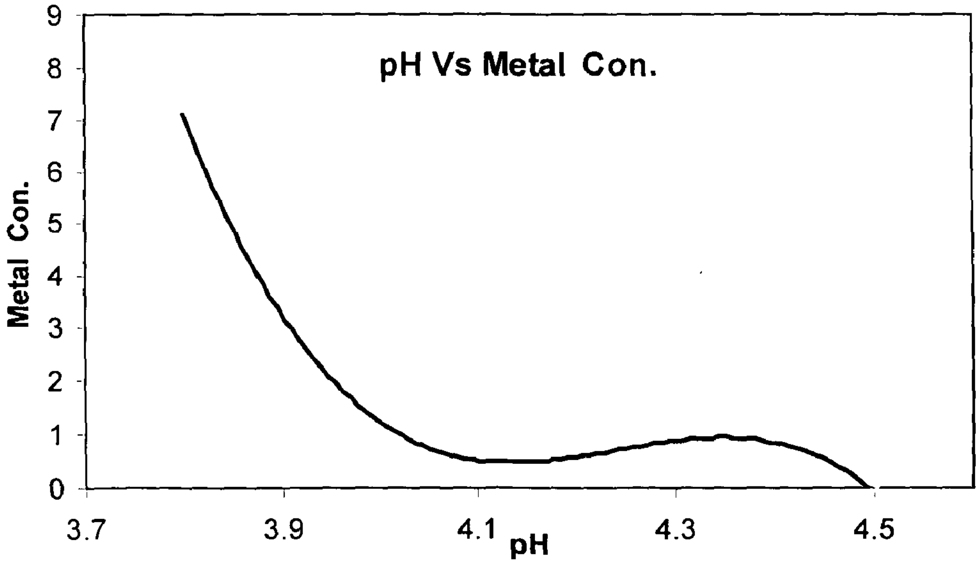


Fig 5.6 pH Vs Metal concentration

Overall Experiment;

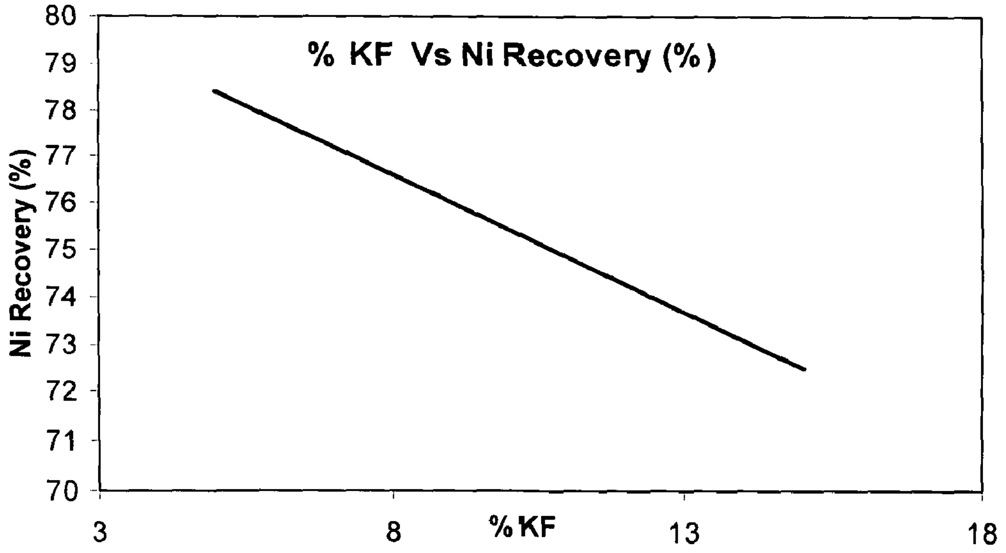


Fig 5.7 % KF Vs Ni recovery (%)

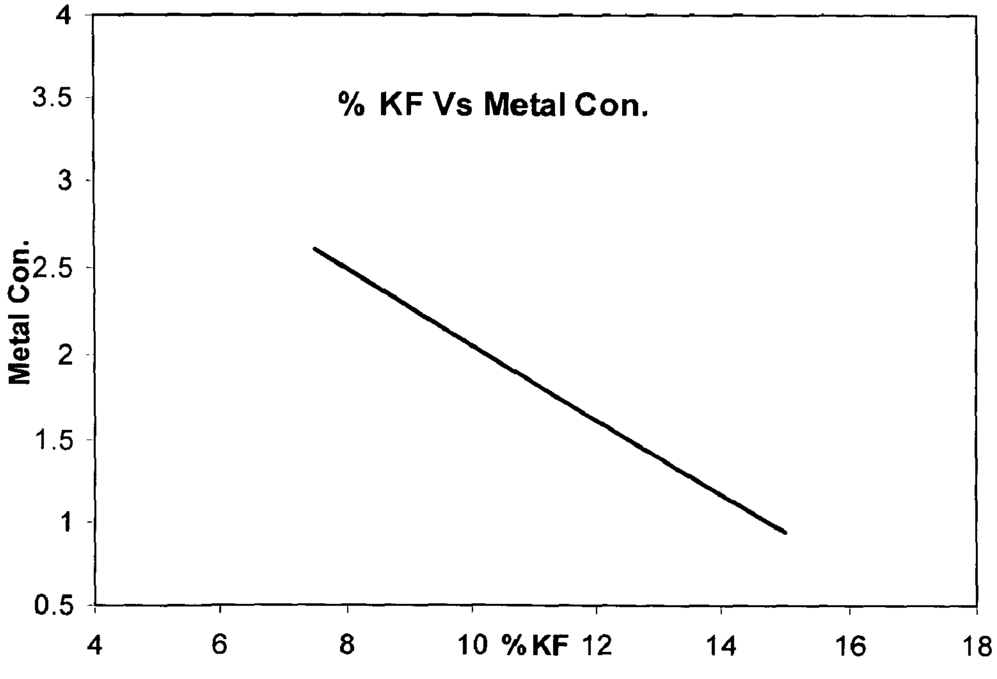


Fig.5.8 %KF Vs Metal concentration

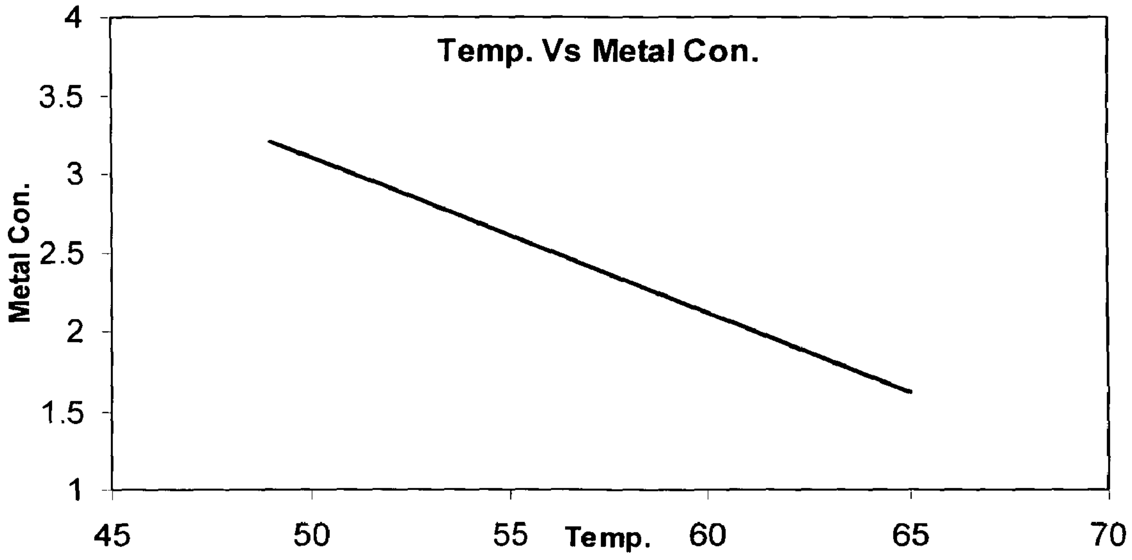


Fig 5.9 Temperature Vs Metal concentration

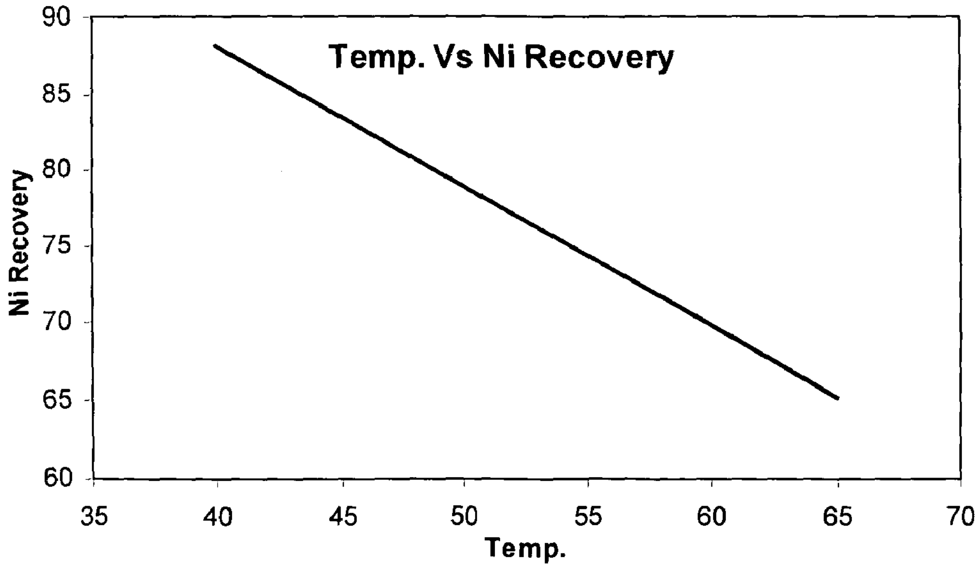


Fig 5.10 Temperature Vs Ni recovery

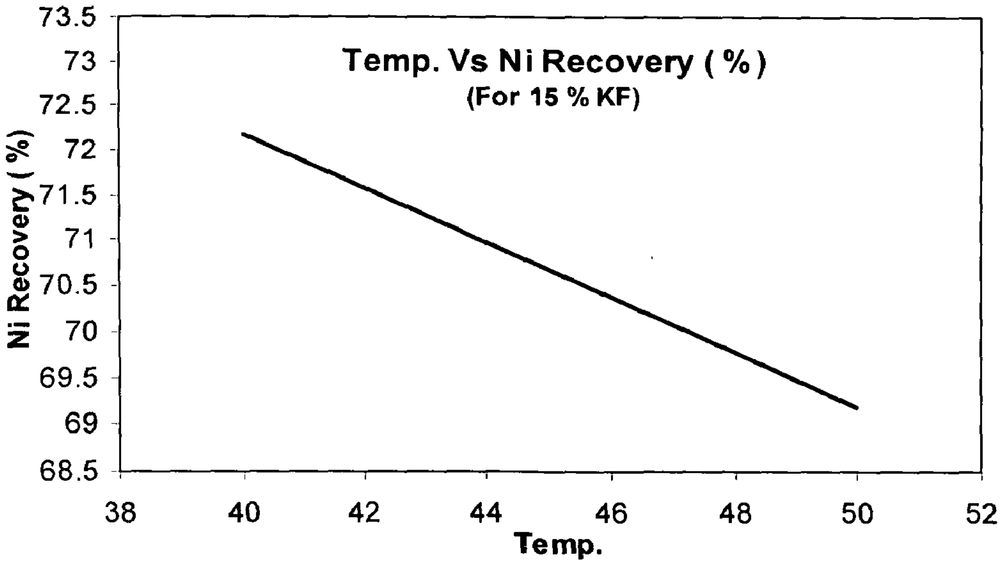


Fig 5.11 Temperature Vs Ni recovery(%)

Table 5.1 Optimum Conditions for Nickel Recovery

Variables	Optimum condition
pH	4.1-4.5
Temp	40-55
%KF in alkali	14-15%

Table 5.2 Experiments at Optimum Conditions

Exp 3	pH	Temp (°C)	%KF	Ni recovery (%)	Ni purity (%)
15	4.5	40	15	74.69	100
14	4.25	40	15	72.75	99.52
10	4.15	52.5	10	77.01	99.37
7	4.05	52.5	10	79.38	97.44
5	4.01	53	10	78.03	97.40
16	4.00	45	15	69.05	97.45

Meanwhile, nickel recovery scarcely varied with temperature when %KF and pH are fixed. Finally, an optimum set of experimental conditions, which provides a nickel recovery of around 74.7% with 100% purity can be deduced from Fig5.11.

Two experiments in these intervals were carried out for the experimental validation of the optimization. Their results are shown in Table 5.2.

As iron oxide precipitates at these conditions, nickel tends to co-precipitate.

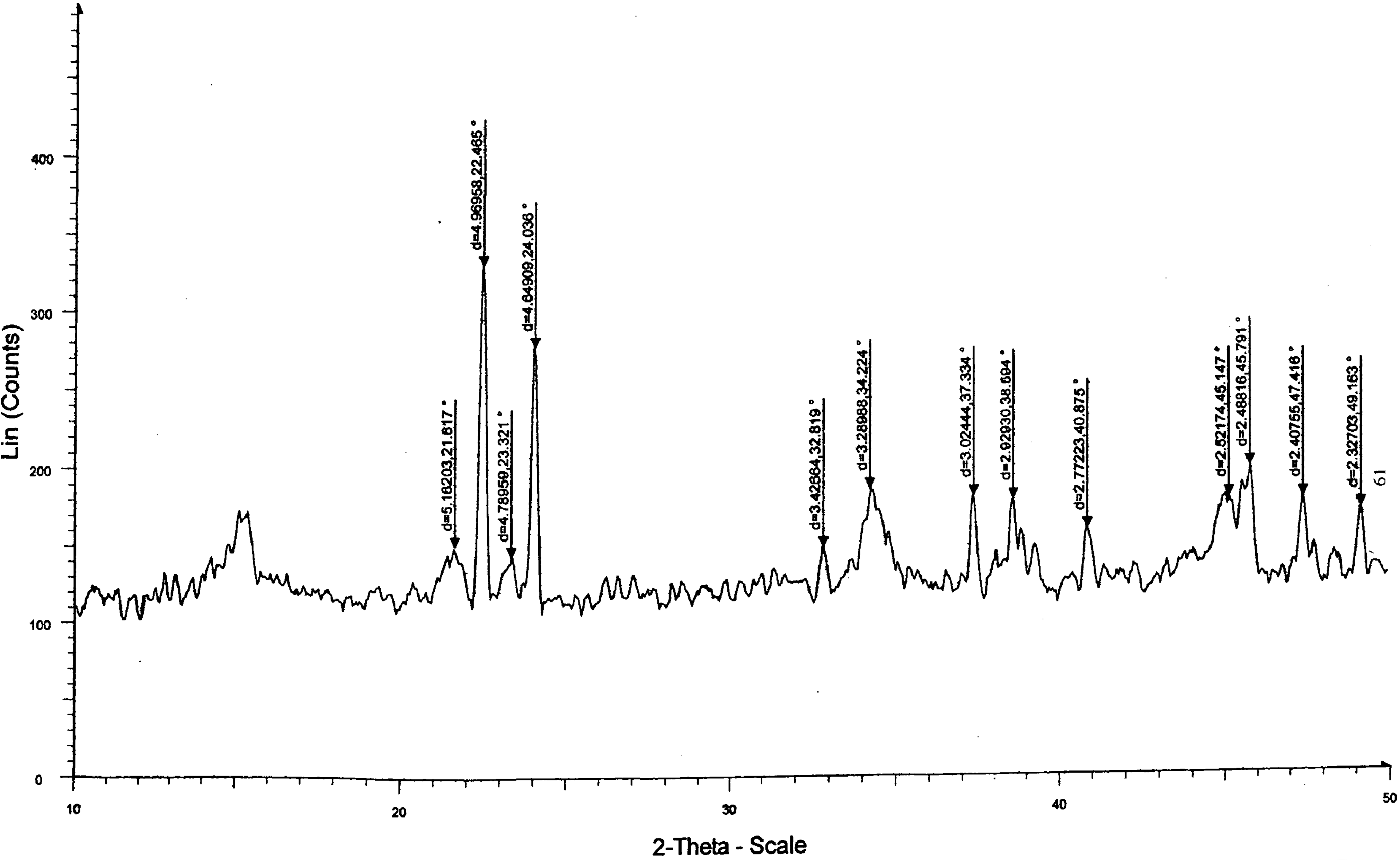
Solid-Phase Characterization;

XRD analysis shows that the main phase in solid product at optimum conditions is dipotassium aquopentafluoroferrate, K_2FeF_5,H_2O in Fig (pages 61-66)). This phase can be accompanied by the nonhydrated one, but it depends on the drying process for analysis. Oxide phases can appear when there is not enough fluoride added to the medium; in Fig, γ-Fe_2O_3 was present. Chromium solid phase is difficult to study because of its low content and the pattern similarity between iron and chromium fluorides. A new experiment was made at optimal conditions where the fed liquor had no iron or nickel, only chromium (III). In this case, pickling liquor was prepared by solving $Cr(NO_3)_3,9H_2O$ in a HF/HNO_3 mixture with the same acidity of real pickling liquors. A diffractogram of the precipitate is shown in Figures (page no 61-66). Hydrated CrF_3 is the main chromium phase.

Table 5.3 Preliminary Experiments of $Ni(OH)_2$ Precipitation

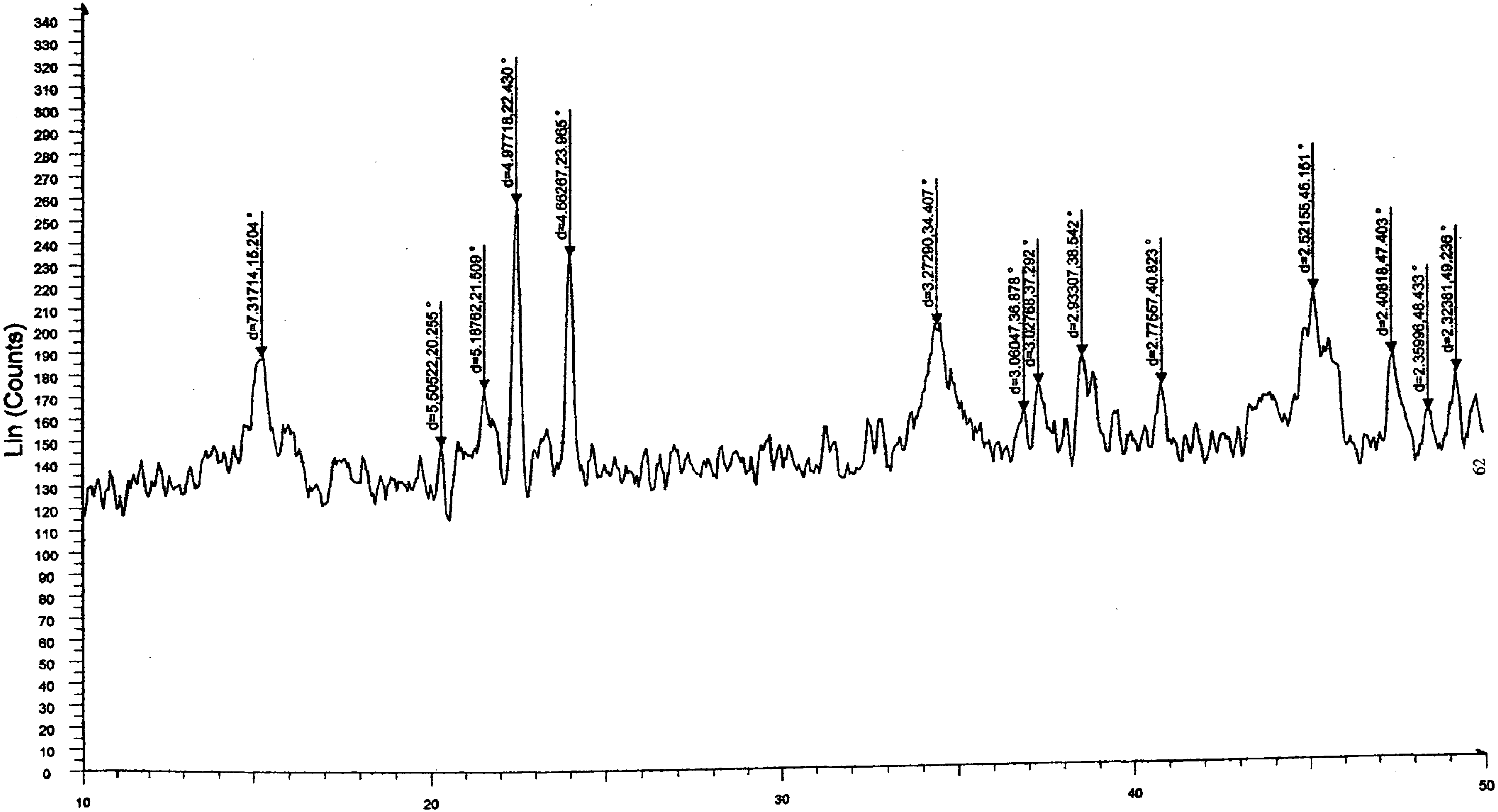
Exp	pH	Temp(°C)	Precipitated Ni(%)
1	9	52	96
2	10	52	97
3	10	59	98
4	10	70	99
5	11	51	100
6	12	50	100

EXP-1 Sample-(9) 1gm



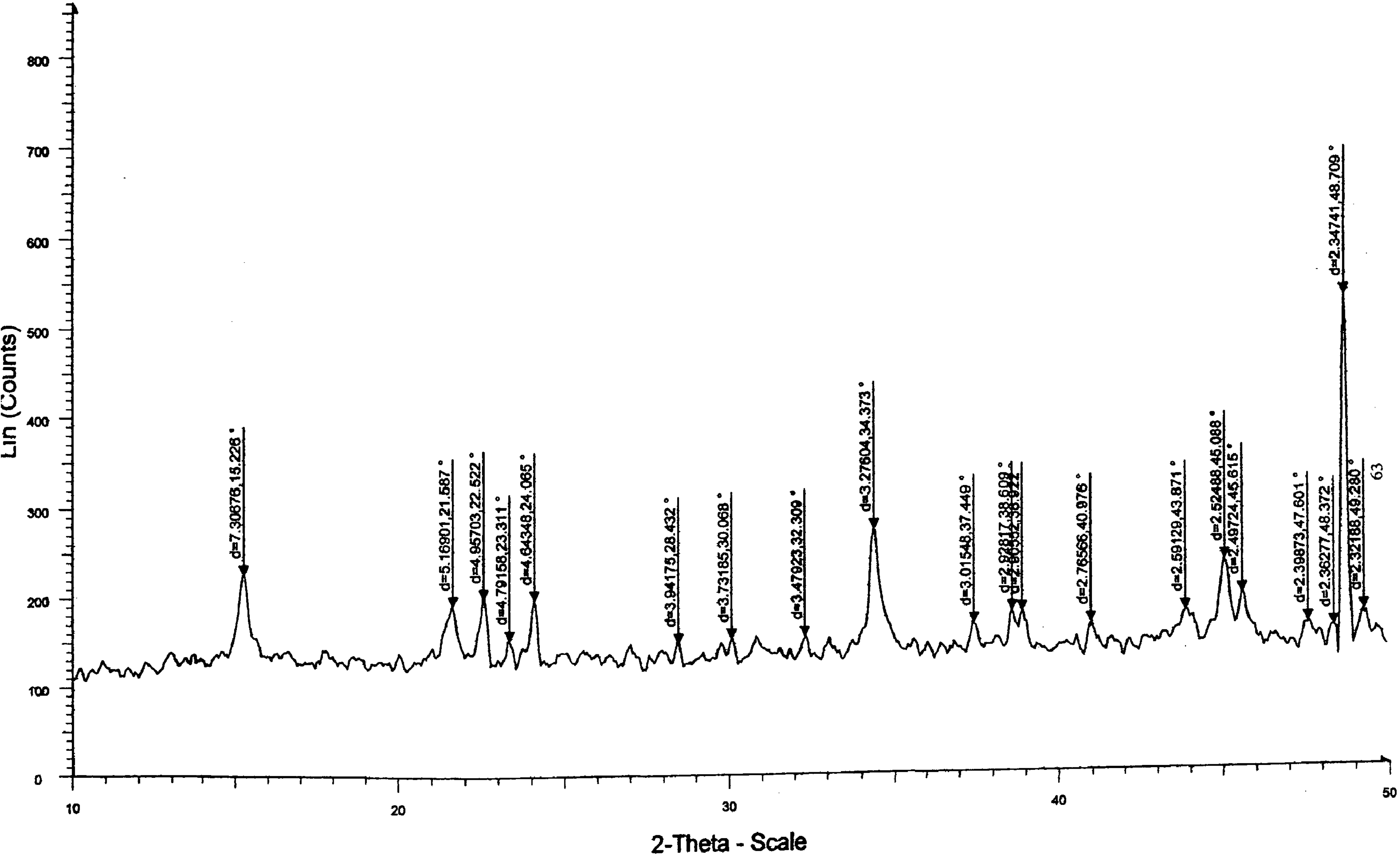
EXP-1 Sample-(9) 1gm - File: EXP-1 Sample-(9) 1gm.raw - Type: 2Th/Th locked - Start: 10.000 ° - End: 50.000 ° - Step: 0.050 ° - Step time: 3. s - Temp.: 25 °C (Room) - Time Started: 1151391744 s - 2-Thet
Operations: Smooth 0.150 | Y Scale Mul 0.708 | Import

EXP-1 Sample-(10) 1gm



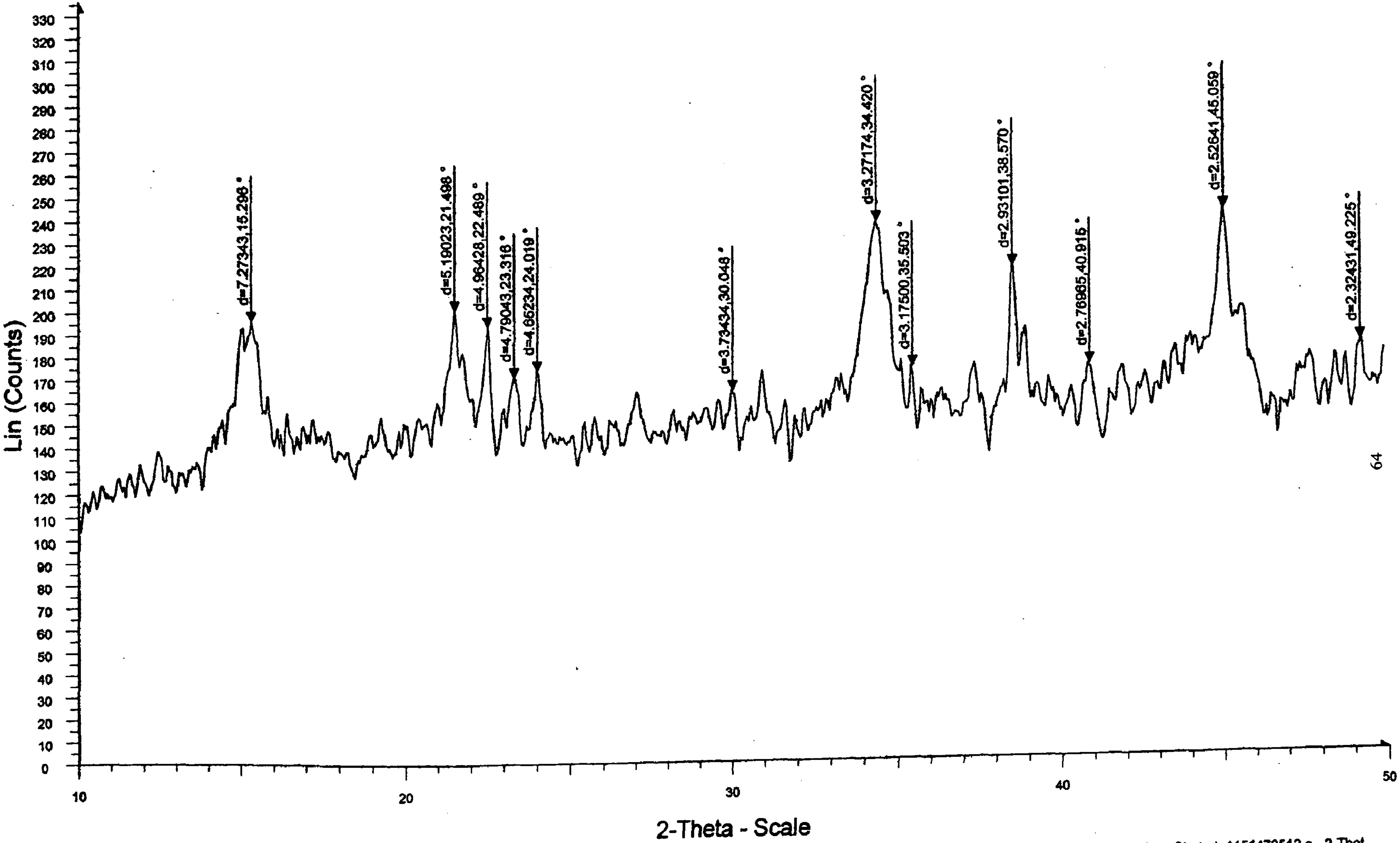
EXP-1 Sample-(10) 1gm - File: EXP-1 Sample-(10) 1gm.raw - Type: 2Th/Th locked - Start: 10.000 ° - End: 50.000 ° - Step: 0.050 ° - Step time: 3. s - Temp.: 25 °C (Room) - Time Started: 1151399424 s - 2-T
Operations: Smooth 0.150 | Y Scale Mul 0.750 | Import

EXP-2 Sample-(15)



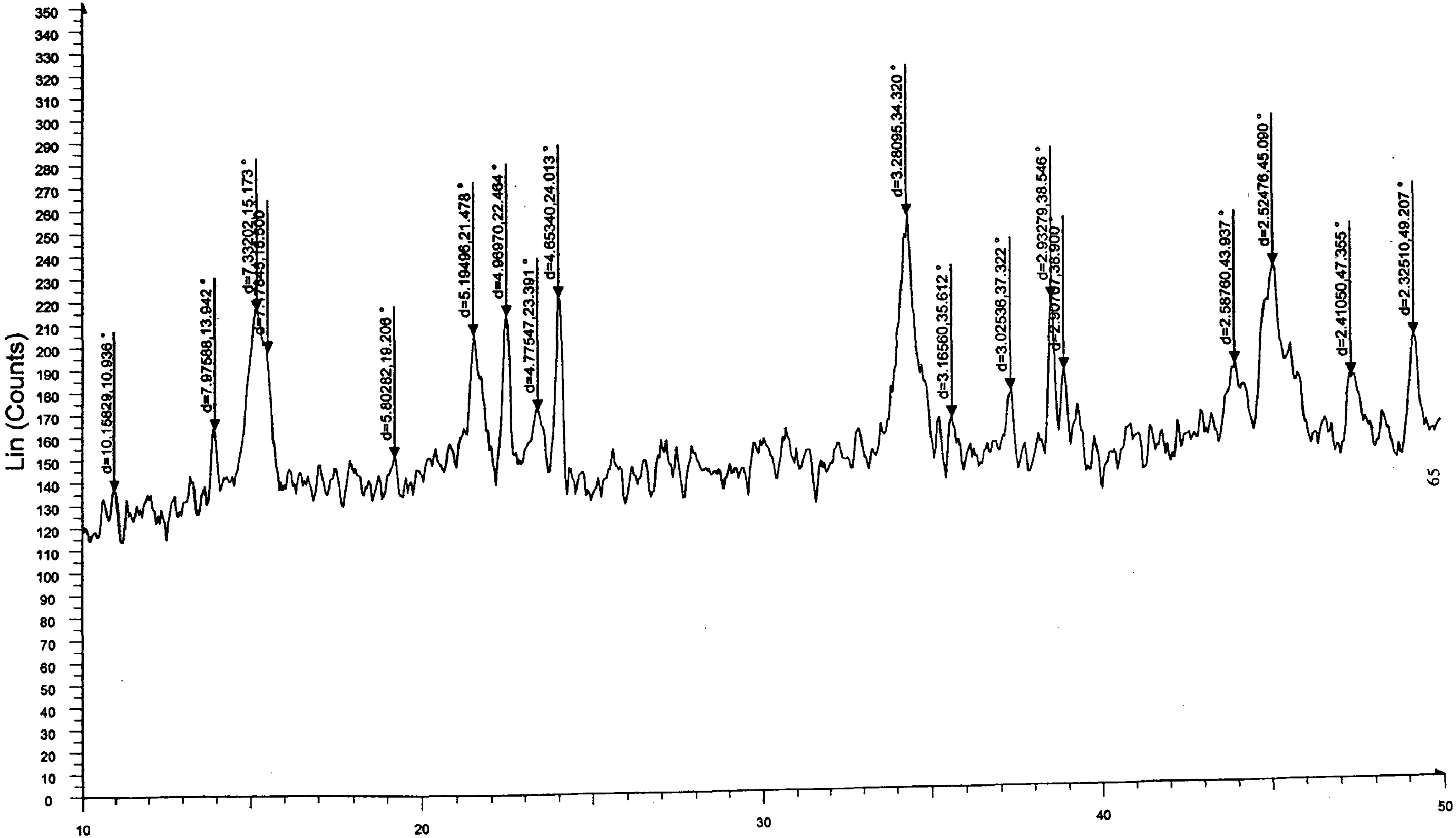
EXP-2 Sample-(15) - File: EXP-2 Sample-(15).raw - Type: 2Th/Th locked - Start: 10.000 ° - End: 50.000 ° - Step: 0.050 ° - Step time: 3. s - Temp.: 25 °C (Room) - Time Started: 1151469696 s - 2-Theta: 10.0
Operations: Smooth 0.150 | Y Scale Mul 0.750 | Import

EXP-3 Sample-(5) 1gm



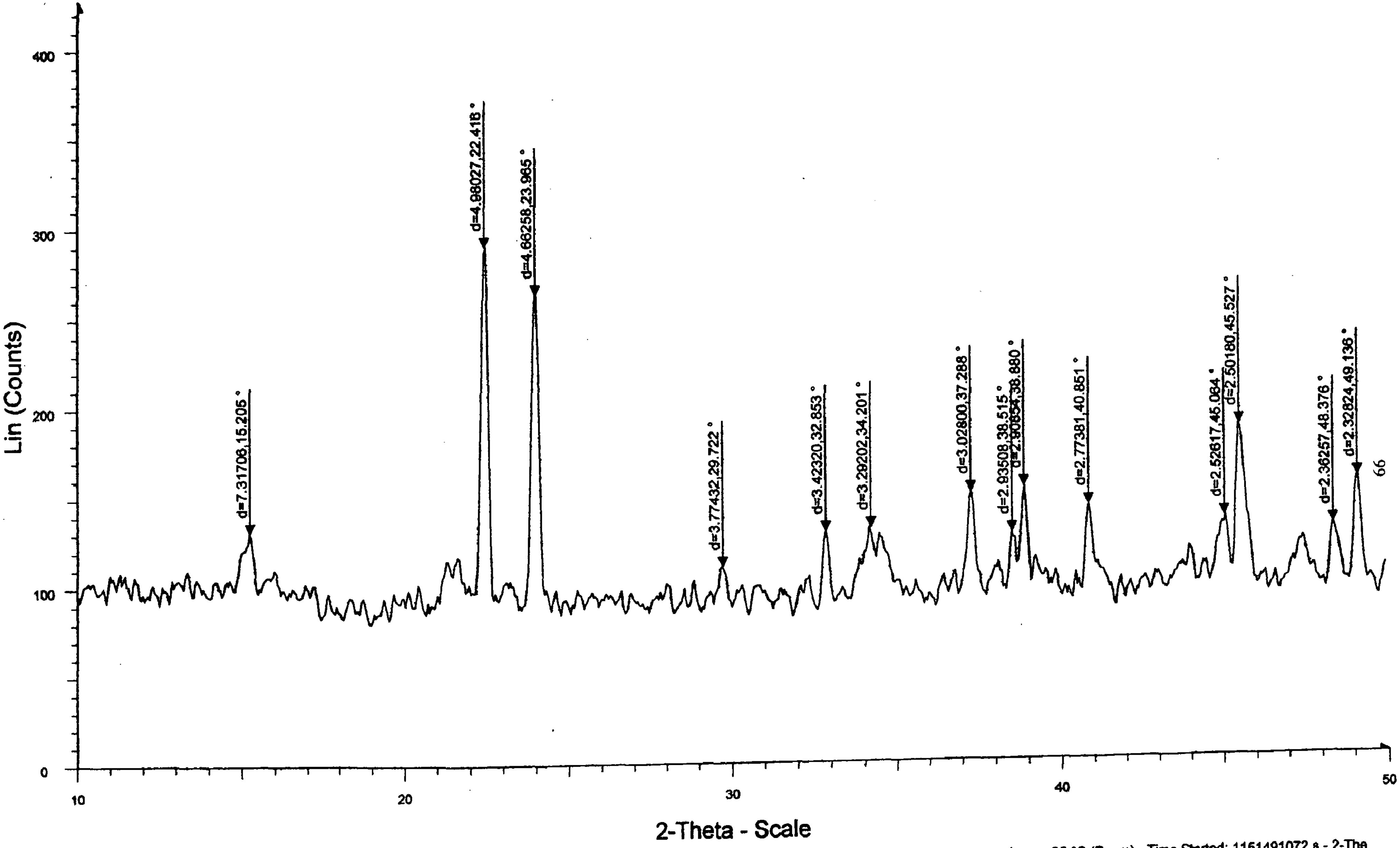
EXP-3 Sample-(5) 1gm - File: EXP-3 Sample-(5) 1gm.raw - Type: 2Th/Th locked - Start: 10.000 ° - End: 50.000 ° - Step: 0.050 ° - Step time: 3. s - Temp.: 25 °C (Room) - Time Started: 1151472512 s - 2-Thet
Operations: Smooth 0.150 | Y Scale Mul 0.750 | Import

EXP-3 Sample-(10) 1gm



EXP-3 Sample-(10) 1gm - File: EXP-3 Sample-(10) 1gm.raw - Type: 2Th/Th locked - Start: 10.000 ° - End: 50.000 ° - Step: 0.050 ° - Step time: 3. s - Temp.: 25 °C (Room) - Time Started: 1151477504 s - 2-T
Operations: Smooth 0.150 | Y Scale Mul 0.750 | Import

EXP-3 Sample-(16) 1gm



EXP-3 Sample-(16) 1gm - File: EXP-3 Sample-(16) 1gm.raw - Type: 2Th/Th locked - Start: 10.000 ° - End: 50.000 ° - Step: 0.050 ° - Step time: 3. s - Temp.: 25 °C (Room) - Time Started: 1151491072 s - 2-The
Operations: Smooth 0.150 | Y Scale Mul 0.708 | Import

5.3 NICKEL HYDROXIDE PRECIPITATION

Liquid effluent from selective precipitation is composed mainly by K^+(60-70 g/L), F^- (5-10 g/L), NO_3^- (50-70 g/L), and Ni^{2+} (2-3 g/L). This stream is fed to a new precipitation stage, where more alkali is added; $Ni(OH)_2$ is obtained in the solid phase, while the effluent, composed of K^+,NO_3^-, and F^-, with traces of metals, is fed to an acid recovery stage. Preliminary results show that, at high pH, more than 97% of the nickel is precipitated as $Ni(OH)_2$ (Table5.3). Solid fluoride content decreases with high temperature and pH; in the case of experiment 27, the low fluoride content implies that solid product of the reaction is recyclable. First XRD analysis of solids show that it is composed mainly by R-$Ni(OH)_2$, while there is no detectable phase containing fluoride.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

ONCLUSIONS

m the present study, the following conclusions are drawn:

1. Nickel hydroxide precipitate by selective precipitation is a good method and it gives very pure Ni as filtrate from that we will separate the nickel by adding alkali to reach the pH up to 9- 10.Iron and chromium is removed by filter cake.
2. Less quantity of chemicals (KOH&KF) required for efficient recovery of nickel hydroxide.
3. This reaction takes less time to produce pure nickel hydroxide(99-100%) at the optimum condition such as pH is 4.1-4.5 ,Temp is 40-50°C and the % KF is 14-15%.
4. No toxic release coming from this process.
5. 100% removal of iron& chromium as precipitates is possible.
6. Experiment procedure also easy and it's not produce the side product except the iron and chromium hydroxide precipitate.
7. Temperature was the most influential variable for chromium concentration.
8. %KF in the alkali solution was the most important variable for iron concentration.

6.2 RECOMMENDATIONS

1. Experiment to continue to achieve 100% efficiency by sodium hydroxide used as alkali.
2. Using ammonium hydroxide to get the same nickel recovery and the efficient removal
3. Other methods for the removal of nickel hydroxide like Total precipitation,sequencial precipitation.

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