



A hydrochloric acid process for nickeliferous laterites



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ABSTRACT

The development of a hydrometallurgical hydrochloric acid based leaching process for the treatment of nickeliferous laterites of various types is described. Work carried out in the Department of Mining and Mineral Engineering, Leeds University, U.K. over a number of years, on the development of a route for treating all types of lateritic nickel ore, is reported in fairly general terms. This paper presents an update on the work carried out and a discussion of a possible final process. Conceptually the process comprises leaching of the ores in azeotropic HCl; counter-current washing to maximise nickel recovery; separation of iron either by precipitation as goethite or by solvent extraction; cobalt recovery by solvent extraction with a tertiary amine; recovery of nickel by solvent extraction followed by electrowinning, hydrogen pressure reduction or pyrohydrolysis and regeneration of hydrochloric acid by pyrohydrolysis with by-product recovery of magnesia some of which might be used for acidity control in the process. Attempts to leach successive batches of ore in a cyclic or counter-current manner to build up metal concentration were unsuccessful due to passivation by formation of a product layer around the ore particles. A key process step is concentration of the nickel in the leach liquor (1–5 g/L) and its separation from magnesium and/or iron to a tenor compatible with recovery methods. This can be achieved using solvent extraction with Cyanex[®]301, Cyanex[®]302 or Versatic 10, the last of which displayed the best extraction characteristics. Cyanex[®]301 showed excellent selectivity for nickel but stripping required high concentrations of acid whilst Cyanex[®]302 showed appreciable co-extraction of magnesium. Whilst some of the process steps have been thoroughly researched, others remain to be proven and it was not possible to test the process as a whole or to carry out an energy balance, so that nothing can yet be stated definitively regarding the economics of the route but some factors regarding energy consumption in pyrohydrolysis are discussed. Relevant up to date literature on chloride based hydrometallurgical processes for laterites has been briefly reviewed. The contributions of individual research workers are acknowledged at appropriate points in the text.

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1. Introduction

Shortly after joining the Department of Mining and Mineral Engineering, Leeds University, it was suggested to me by an external advisor (Noakes, 1970) that novel methods for processing nickel laterite ores should be investigated. Because of the relative ease of separating some of the component metals in chloride medium and of recycling HCl as in the Falconbridge Matte Leach Process (Archibald, 1962; Thornhill et al., 1971; Wigstøl and Frøyland, 1972), it was decided to investigate a route based upon hydrochloric acid leaching and able to treat all types of lateritic nickel ore. This paper describes in fairly general terms work done by several generations of research and final year students who

contributed to the development and understanding of the various unit operations in the flow sheet and updates the conclusions in the light of recent literature.

2. Processing of lateritic nickel ores

Nickeliferous laterites occur as two main types that differ in iron, silica and magnesium content. They are the weathering products of ultrabasic rocks and different forms often appear in several horizons of the same deposit. They are distributed worldwide, mainly in tropical areas (de Waal, 1971; Canterford, 1975). It has been estimated (Bleiwas, 1991; Davidson, 2006) that about 70% of the world's nickel reserves comprise this type of ore but only about 45% of total production comes from this source owing mainly to the complexity of the ores, the difficulties in processing and the high energy requirements as compared to exploiting sulphide ores.

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Processes have been described by Boldt and Queneau (1967) and reviewed by Canterford (1975), Monhemius (1987) and King et al. (2005). Anthony and Flett (1997) who also reviewed the technology for nickel production from both lateritic and sulphide ores.

The main methods that have been used include direct smelting of the ore to either matte or ferronickel in electric arc or blast furnaces; reduction roasting followed by either ammonium carbonate leaching (Caron process), (Caron, 1924, 1950) or sulphuric acid leaching under pressure (Moa Bay process), (Carlson and Simons, 1960; Whittington and Muir, 2000). Many other processes have also been proposed. Some methods are preferable for one type of ore whilst others work better on different types and where the deposit consists of several different types of ore complex flowsheets can result.

Limerick (1978) attempted to correlate mineralogical factors with the response of a lateritic nickel ore to either direct HCl leaching or to aqueous chlorination of reduced ore (Roorda and Queneau, 1973). He concluded that chemical composition is a poor guide to the likely response to a particular process and that the measured value of a mineralogical parameter need not necessarily correlate with the measured response of the sample. Quantitative correlations between mean mineralogical parameters and process response were not generally practicable except where only a few properties significantly affected process efficiency. HCl leaching was such a process.

In general, however, silicate ores (sapolite or serpentinite) are usually treated by pyrometallurgy whereas hydrometallurgical techniques like the Caron and Moa Bay processes seem more suitable for limonites especially if the magnesia content is low. These processes consume less energy than pure pyrometallurgy but extraction of nickel from serpentine ores is not efficient. de Graaf (1979a,b) studied the applicability of the Caron process to high silica ores and showed that the control of reduction conditions was critical for efficient nickel recovery and iron separation. Sulphuric acid pressure leaching of high magnesia ores gives rise to high acid consumption and difficult high temperature recycling to recover the acid from magnesium sulphate. O'Kane (1979) estimated that direct pyrometallurgical treatment requires about 40 times the amount of energy for the same amount of metal as from a sulphide concentrate. Other processes require somewhat less energy but still use a large excess over sulphide processing (Dasher, 1971; Blanco and Holliday, 1981). O'Kane (1979) also illustrated that the recovery of cobalt can significantly improve the economics of processing lateritic ores. This applies principally to hydrometallurgical routes, since pyrometallurgical routes do not attempt such a recovery. Taylor (1996) noted a growing interest in the high pressure sulphuric acid leach (HPAL), which, based on the modifications by AMAX (Berezowsky, 1997), is estimated to be the most energy efficient of the laterite processes. In addition, sulphide deposits are blessed with by-product metals such as copper, cobalt, gold, silver, and the platinum group metals, whereas cobalt is the only by-product associated with laterites. Recently heap leaching with H₂SO₄ has become a popular approach at many locations and Wedderburn (2009) has reviewed the status and economics of over 30 nickeliferous laterite projects with particular reference to the use of heap leaching. Tsuchida (2015) has presented an updated review of HPAL processes.

Nitric acid was tried unsuccessfully as a leaching agent for U.S. laterites (Harvey and Hossain, 1980) but a nitric acid based process involving recycling of the acid and able to treat all types of ore has been developed recently by Direct Nickel (DNi) (McCarthy and Brock, 2015). Dry and Harris (2012) analysed and compared the economics of processes based on H₂SO₄, HCl and HNO₃ leaching using mass and energy balances to estimate costs. HCl and HNO₃ were less costly than HPAL due to recycling of the reagents. Energy consumption was the major factor.

Taylor (2014) and Dry (2014, 2015) have reported technical and cost comparisons of various laterite treatment processes. This series of papers examined the economics of processing a hypothetical nickel–cobalt laterite using commercially applied processes and also two processes still under development. Part 1 outlined the processes and their applicability to limonite and sapolite ores. Part 2 presented results of process modelling to quantify reagent and utility requirements and to calculate the variable portion of the operating costs. Part 3 extended the comparison to fixed operating and capital costs and used simple financial modelling to compare the different processes. The established hydrometallurgical processes were: Pressure acid leaching; enhanced pressure acid leaching; agitated tank leaching at atmospheric pressure; heap leaching and Caron reduction roast/ammonia leach. The pyrometallurgical processes were: rotary kiln calcination with electric furnace smelting; sintering with blast furnace smelting and sintering with submerged arc smelting. These developing technologies were: Neomet (HCl leach, Harris and White, 2011) and DNi (HNO₃ leach, McCarthy and Brock, 2015). The hydrometallurgical and the developing processes were assumed to produce nickel and cobalt as intermediate products (mixed Ni–Co hydroxide or NiO and CoS in the Caron process). The pyrometallurgical processes were assumed to produce nickel in metallic iron, i.e. ferronickel or nickel pig iron.

Pressure acid leaching appeared to offer the best economics for treating limonite if the Neomet and DNi processes did not produce saleable by-products. If by-product hematite and magnesia were saleable, particularly if the hematite could be sold for more than the price of iron ore, the Neomet and DNi processes looked distinctly superior. Of the established processes for sapolite, heap leaching would appear to offer the best economics, but if the by-products were saleable Neomet would offer better economics. Pyrometallurgy appeared to be economically inferior to the hydrometallurgical processes.

3. Original concept for a hydrochloric acid leaching process

The scope for developing a laterite process whereby high purity nickel and cobalt are recovered at reduced energy expenditure is, intuitively, greater using hydrometallurgy. There is therefore a place for such a process capable of treating several different ore types by a single flow sheet without the need for preliminary thermal treatment, high pressure or high energy consumption and if possible with a closed cycle to regenerate acid which would be of environmental benefit. Despite its poor selectivity hydrochloric acid leaching seemed to offer the potential for such benefits though no economic assessment of the process has been attempted here.

Fig. 1 shows the original conceptual flow sheet (Rice and Strong, 1974). From this it is clear that maximisation of the nickel concentration in the leach liquor would be very important for efficient recovery and recycling of the acid using pyrohydrolysis the regeneration of HCl from metal chloride solutions, particularly MgCl₂ at relatively low temperatures (Connors and Butcher, 1971). Drying, reduction roasting or pressure leaching are unnecessary and there is a perceived energy advantage over the conventional pyrometallurgical routes especially for low nickel grade ores. Nickel and cobalt recoveries are high and iron removal and by-product cobalt separation easy in chloride media. A key step in such a process is the separation of the dilute nickel content of the leach liquor (1–5 g/L) from the large excess of magnesium and/or iron and its concentration to a nickel tenor compatible with recovery methods.

3.1. Chloride based processes – literature survey

Hubler and Archibald (1938) patented a process for leaching high Mg % ore in cold 4 to 20% HCl continuing leaching to acidity

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