Introduction Nickel (II)-ion is a major constituent in local galvanic or nickel hydrometallurgy wastes. Although metallic nickel is known to activate hydrogen and is used as a hydrogenation catalyst. There are may be the potential sources of nickel - content raw materials. Traditionally, the Ni2+ in solution has been reduced by electric current or cementation with hydrogen of ammoniacal solution under pressure at elevated temperatures in mechanically agitated autoclaves [1,2]. However, all of the methods require a pretreatment step in which the concentration of nickel (II) is increased. The reduction process flows with high efficiecy (99% and more) only in narrow concentration interval. Other possible alternative to electrowinning and reduction by hydrogen is cementation with aluminium powder as reductant. The present study investigates the cementation of nickel from ammoniacal solution by using aluminum powder in order to increase the cementation rate, as the friction removes passivating layers on the aluminium particles, thus allowing it to be a more powerful reducing agent. Experimental The experiments were carried out in a thermostatted cell with a volume of 250 ml at constant stirring rate (250 min-1). According to the conditions of hydrometallurgy the cementation process was investigated at 20°C using nickel solution of 10-2 M NiCl2. Purified nitrogen was passed through the solution via a dispersion tube to maintain an oxygen-free environment. During the kinetic investigation aliquots of 4 ml were taken and analyzed for nickel using atomic absorption spectroscopy and complexonometry. The cementation deposits were removed, washed with twice-distilled water, ethylalcohol, dried at room temperature under vacuum (-10-1 MPa) and prepared for X-ray phase analysis. Some deposits are leaching in sodium hydroxide solution (3,0 M). In order to evaluate the parameters of time, temperature, solution composition and amount of reducing powder, standard cell charges and operating conditions were chosen as listed in Table 1. Al usage and Ni recovery were calculated from the initial and final metal weights, based on 2/3 mol of Al dissolving per 1 mol of Ni cemented from solution. Table 1 - Standard reagent charges and operating conditions Reagent charges Operating conditions NiCl2·6H2O 0,01 M NH3·H2O 1,50 M NaOH 0,06 M Al powder (~80 mm) 0,013 M temperature: 20°±10C reaction time: till 1 hour agitation: 250 RPM Results 1. Time The test run time was varied from 1 to 90 min, using otherwise standard conditions. As show by Fig.1, there is considerable recovery for the first 5 min, after which recovery decreases steadily and improves to 99,9% after 15-20 min. Beyond 30-40 min however the process is attenuated. Fig. 1 - Time versus % Ni recovery at standard conditions and charge composition 2. Aluminum powder Fig.2 shows the effect of the amount of Al in the charge on Ni recovery for standard conditions. The standard charge of 0,013 M Al was chosen such that 50% of it would have had to react to achieve 100% Ni cementation from 0,01 M Ni2+ solution. The rate of Ni recoveries were linearly related to Al powder input. The dimension of aluminum particles is above 80 mm and its purity is higher than 99,0 %. Fig. 2 - Aluminum powder versus % Ni recovery at standard conditions 3. Solution composition The ammonia forms nickel complexes as follows: NiCl2 + nNH3 = Ni(NH3)nCl2, n = 1-6 (1) The half cell reactions were analyzed to determine if such a process were theoretically possible for the facility in question the half cell reactions are as follows [3]: Al + 4 OH- - 3 e ® [Al(OH)4]- +2,35 V (2) [Ni(NH3)n]2+ + 2 e ® Ni + nNH3 - 0,45 V (3) Since the sum of the oxidation reduction potentials is positive, a reaction is theoretically possible. The concentration of ammonia and NaOH were varied above and below the standard composition and the results are displayed in Fig. 3, 4. As expected from the Ni solubility data, recovery is higher with increased ammonia concentration. In addition Ni recovery is sensitive to NaOH concentration. At higher alkali concentration the sensitivity of recovery rate to it were diminished because Ni(OH)2 is formed. The optimum value for the NH3 : Ni ratio for rapid reduction with 100% efficiency has been found to be 50; this can be seen from Fig.4. Fig. 3 – NaOH : Ni2+ ratio versus % Ni recovery at standard conditions Fig. 4 - NH4OH:Ni2+ ratio versus % Ni recovery at standard conditions 4. Temperature Reaction temperature has a large impact on the recovery rate, as shown in Fig.5. Between 20 - 60°C recovery improves as temperature increases. An Arrhenius plot (Fig.5) over the temperature range of 20 to 60°C revealed that the apparent activation energy is approximately 15 kJ/mol, which is consistent with diffusion kinetics being the rate-limiting step. Over 60°C the cementation is accompanied by formation of Ni(OH)2. Fig. 5 - An Arrhenius plot of Ni cementation by dispersed aluminum using standard condition and charge composition Discussion For the testwork one dimensioned Al powder was used. The reaction rate increase with the concentration of NaOH at the high concentration (0,10 M) form Ni(OH)2. Ammonia solution may be as is used for the hydrogen reduction of Ni. Nucleation is usually defined as the formation of the smallest thermodynamically stable particle (nucleus) of a new phase from the parent phase. In that case nucleation is heteronucleation where the initial deposition of nickel takes place on the surface of aluminum particles. This indicates that the actual reduction reaction is as follows: 3[Ni(NH3)n]2++2Al+8OH–=2[Al(OH)4]–+3Ni+3nNH3 (4) Equation 4 is the combination of equations 2, 3. It would appear that more than a stoichiometric amount of aluminum would be needed to precipitate out all the nickel. However, as shown in Fig.3 a minimum amount of aluminum is necessary for effective treatment. This is a result at least in part of a competing reaction. The aluminum will also react with the caustic and water to form hydrogen as shown by the following: 2Al + 2NaOH + 6H2O = 2Na[Al(OH)4] + 3H2 (5) In the works [4,5] at the pH range from 10 to 13 the aluminate ion is shown to be a polymeric anion of composition in which the [Al(OH)4]- units are linked together by two or more hydroxyl bridges. That system is metastable and during some time the polymeric anion is destroyed and the bayerite is formed as sol [5]. The reduction rate of the reaction above will depend upon the surface area of the particles which present and also upon the growth kinetics, which involve the diffusion of nickel ion to the surface of the growing metal particles and chemical reactions at the surface. The rate of reduction and the yield are functions of temperature, amount of aluminum, alkali and ammonia used, and their concentrations. Usually the cementation process describes by the first order kinetic equation [6]. It is evident that all experiments were analyzed with the following relation [6]: dCNi/dt = K.S.CNi, where S is the active surface area (cm2), K - the specific rate constant (s-1) and CNi - concentration of nickel ions, mol/l. However the reduced nickel is deposited on the surface of the aluminum already present, causing growth of the solid particles. Nickel metal ions in solution can be reduced by aluminum only when the pH is higher than a 11 value. Agglomeration between the growing metal particles during reduction is an important matter because it will affect the surface area available for growth. Since the product or the reduction is metallic nickel, the total catalytic surface should increases as the reaction proceeds. However, the reduced nickel is deposited on the surface of the initial nickel already present, causing growth of the solid particles and the growth of reaction rate falls. Factors causing retardation of the reaction are following: 1) The specific adsorption of colloidal bayerite particles and ammonia molecules on the aluminum surface [7], thereby decreasing the effective surface area. 2) The tendency of nickel particles to agglomerate causes a decrease in the catalytic surface. 3) When starting with an NH3 : Ni, ratio greater than 50, the ratio of excess ammonia to remaining unreduced nickel will increase and the stronger complexation will reduce the concentration of free nickel ions. This will cause the reduction rate to slow down when the free nickel ion concentration grows higher than a certain value. The X-ray analysis has shown that the deposit consist of about 20 % of aluminum and 80% nickel . The diffraction lines have been indexed in Table 2 and are of face-centered cubic nickel and aluminum. Likewise a small volume of hydrogen may be absorbed in the form of NiH2. The planes 110, 111, 200, 220, 311 are equally exposed on the surface of the solid (Table 2). Table 2 - The results of X-ray analysis Experimental data Reference data (ASTM) [8] Ni Al d, Ao J, r.unit. d, Ao J, r.unit. hk l d, Ao J, r.unit. hk l 2,341 23 2,338 100 111 2,035 100 2,034 100 111 2,024 47 200 1,762 20 1,762 42 200 1,432 7 1,431 22 220 1,246 11 1,246 21 220 1,222 8 1,221 24 311 1,170 2 1,169 7 222 Conclusions Ni concentration with Al powder takes place in three stages: 1) instantaneous cementation on elemental Al; 2) slower Ni cementation reaction at first order across a film of Al(OH)3 and a stage of Ni dissolution. It is possible to prevent or counteract the redissolution stage in the batch tests by decreasing the pH or increasing free cyanide concentration. In continuous tests redissolution dissappears within a few minutes of experimentation due to the friction that eliminates the passivated film on powder Al. If the pH or free NH3 concentrations are low during the first two concentration stages the cementation rates in both stages are large. If the pH and the free NH3 concentrations are simaltaneously lowered the formation of the hydroxide ion is prevented and Al is comlexed by OH- transfer from NiNH3 - ions. With this a maximum consumption of NH3 and alkali and less Al oxidation could result. Cementation is controlled by diffusion during the second stage. For this reason the cementation rate increases when the frequency increases thus counteracting the effect of the passivated film. An increase in temperature does not affect the cementation rate at any stage because in the first stage, temperature favors redisolution and in the second stage the process is controlled by diffusion, which is less affected by temperature. The cementation of Ni from ammonia solution with Al powder is a technically viable process. The reaction rate is high at or below 20°C, and kinetic are diffusion-controlling from 20 to 60°C. As shown the experiments the Ni(OH)2 is mainly precipitate at temperature over 600C. The best Ni yield is achieved with a maximized alkali concentration, but lower then 0,10 M and fixed in a narrow range of ammonia concentration. The reaction rate is seen to be approximately directly proportional to the concentration of aluminum powder used for seeding. The diminish effect at higher concentrations might be due to the difficulty of maintaining larger quantities of metallic aluminum in suspension. A recovery of as much as 99% of Ni in a maximum time of 1 min. is obtained in the batch tests. Peak nickel recovery from ammoniacal solution (0,01 M) was achieved at 600C; CNH3 ³ 1,5 mol/l; 0,05 £ CNaOH 0,10 mol/l, CAl ³ 0,013 mol/l (CAl/ CAlst ³ 1,6 g/g).