

## CAPITALIZATION OF SPENT NiO/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> CATALYSTS

### 4. NICKEL OXIDE LEACHING MECHANISM

**Lucian Gavrilă**

*Depollution Engineering Laboratory, University of Bacău,  
Calea Marasesti 157, RO-5500 Bacău, Romania,  
e-mail: lgavrila@ub.ro*

**ABSTRACT:** Kinetic data concerning nickel oxide acid leaching from spent steam reforming catalysts are presented. Based on this data, a sigmoid model that describes nickel dissolution is presented. The model reveals that two steps are involved in Ni leaching: a first one with a time increasing reaction rate, corresponding to free NiO dissolution, and a second one with a time decreasing reaction rate, attributed to the dissolution of the nickel oxide entrapped in the alumina crystalline structure.

**KEYWORDS:** *nickel, catalysts, spent catalysts recovery, steam reforming catalysts, leaching mechanism.*

## INTRODUCTION

Recycling, reuse or capitalization of spent catalyst from different areas (chemical industry, oil refining, etc.) is necessary at least from an environmental view point, unless economical benefits could not be achieved. While literature abounds in "recipes" for nickel reclaiming from the rich nickel spent catalysts [1 - 6], there is a lack of kinetic data, needed for designing rational recovery technologies. It is also known that, till now, there is no available technology able to process economically spent catalyst with low content (below 10% mass) of nickel and cobalt, these catalysts being piled in abandoned oil refineries, waiting for further processing [7 - 13].

The aim of the paper is to bring several kinetic data regarding to the acid leaching of low nickel content spent steam reforming catalysts, and to suggest a nickel dissolution mechanism.

## EXPERIMENTAL

The tested spent catalyst is a steam reforming catalyst consisting in NiO on a  $\alpha$ - $\text{Al}_2\text{O}_3$  support. The catalyst has been sampled from an industrial ammonia plant after about 20,000 hours in operation. The main characteristics of the catalyst are shown in Table 1.

*Table 1. Characteristics of the spent steam reforming catalyst*

Characteristic	Value
Apparent density, $\text{kg.m}^{-3}$	1881.67
Bulk density, $\text{kg.m}^{-3}$	780.70
Axial compression strength, MPa	10.06 - 19.80
Nickel (NiO) content, mass percent	5.87 (7.47)*
Aluminum ( $\text{Al}_2\text{O}_3$ ) content, mass percent	36.42 (68.82)*
Insoluble in aqua Regis, mass percent	3.21

\* - for the fraction with  $0.04 \text{ mm} < d_p < 0.10 \text{ mm}$

The catalyst average sample was grounded, milled and sorted, the granules having the diameter  $0.04 \text{ mm} < d_p < 0.10 \text{ mm}$  being used for the kinetic study. A laboratory installation containing a thermostated batch stirred tank reactor was used for leaching the catalyst with sulfuric acid solutions. The installation is described in [14] and the working technique in [15]. Parameters kept constant during tests are shown in Table 2, their values being previously established [16, 17].

*Table 2. Constant parameters in the acid leaching process*

Parameter	Value
Sulfuric acid initial concentration, mass percent	60
Catalyst particles average diameter, mm	0.07
Liquid : Solid ratio (LSR), mL/g	50
Mixing revolution, rpm	600

The influence of temperature (293 - 368 K) upon the nickel dissolution degree ( $\eta_{\text{NiO}}$ ) has been studied. The nickel dissolution degree has been defined as [15]:

$$h_{\text{NiO}} = \frac{M_{\text{NiO}}}{M_{\text{Ni}}} \cdot \frac{\text{LSR}}{\bar{x}_{\text{NiO}}^0} \cdot \bar{C}_{\text{Ni}^{2+}} \cdot 10^{-3} \quad (1)$$

## RESULTS AND DISCUSSIONS

Based on the experimental measured nickel ions concentration from the liquid phase [18], the  $\eta_{\text{NiO}}$  values have been calculated and the time - dissolution degree curves for different temperatures have been drawn (Figure 1).

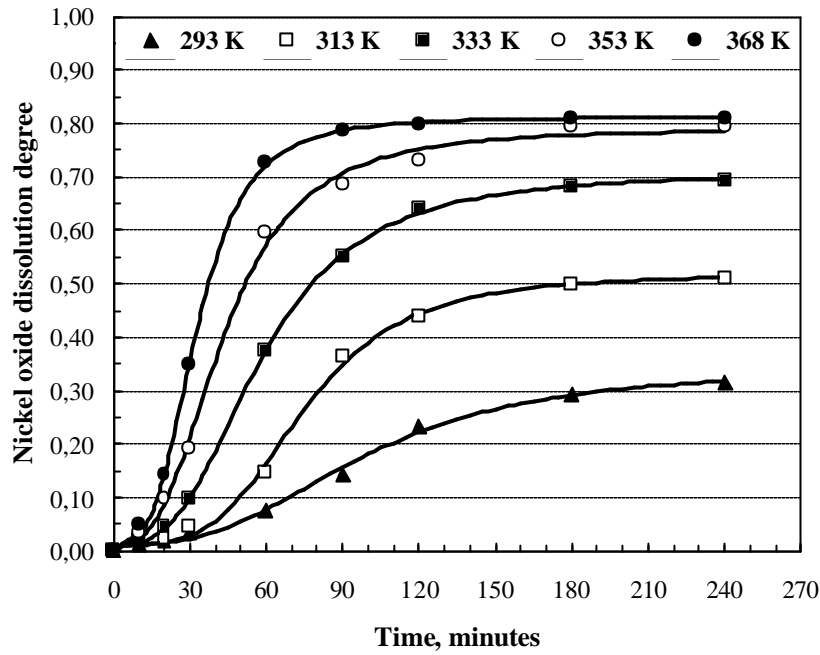
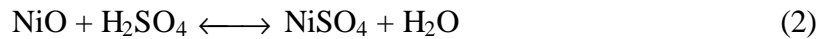


Fig. 1. Primary kinetic curves  $\eta_{\text{NiO}} - t$

Apparently, the nickel oxide dissolution occurs fast, without being influenced by the dissolution of the alumina from the catalyst's support [18, 19]. Nevertheless, the particular shape of the kinetic curves allows us to analyze in-depth the catalyst acid leaching mechanism. The kinetic curves that describe nickel dissolution have a sigmoid shape, shape that accentuates with the temperature. It is obvious that the higher the temperature and the longer the reaction time, the greater the nickel dissolution degree. At long enough reaction times, regardless the temperature,  $\eta_{\text{NiO}}$  trends to a constant value. It seems that the equilibrium of the reaction:



is going to be reached. As it can be seen from graph, the equilibrium is reached before all the NiO from the spent catalyst is dissolved in the acid environment. About 20 to 50 percent of the nickel from the catalyst is bonded in more stable and less reactive structures than NiO.

The sigmoid shape of the  $\eta - t$  curves indicates that nickel dissolution occurs in two steps:

- in the first step, the reaction rate increases to a maximal value (corresponding with the inflexion point of the kinetic curve);
- in the second step, the reaction rate decreases to zero (corresponding to the horizontal part of the curve, where  $\eta_{\text{NiO}} = \text{constant}$ ).

Using the CurveExpert® computer simulation program [20], a sigmoid equation with four parameters was chosen as the best fit for the experimental  $\eta - t$  data. The equation, known as the "MMF Model" could be written as:

$$h_{\text{NiO}} = \frac{a \cdot b + c \cdot t^d}{b + t^d} \quad (3)$$

where a, b, c and d are constants specific to each kinetic curve (Table 3).

Table 3. Parameters  $a - d$  from equation (3)

Temp. [K]	$a \times 10^3$	$b \times 10^{-6}$	$c$	$d$	$R^2$
293	10.964766	0.3940978	0.34307442	2.8073622	0.9978
313	17.017204	24.606017	0.51452975	3.9373804	0.9987
333	9.865436	0.12969573	0.70756738	2.8985886	0.9998
353	11.713538	0.05443033	0.79034072	2.8932601	0.9987
368	17.062014	0.13631437	0.81134274	3.3871209	0.9997

Figure 2 presents the  $\eta - t$  data plotted according to the MMF sigmoid model (lines) compared with experimental data (points). As expected (due  $R^2$  values greater than 0.995) a very good theoretical - experimental correlation can be observed.

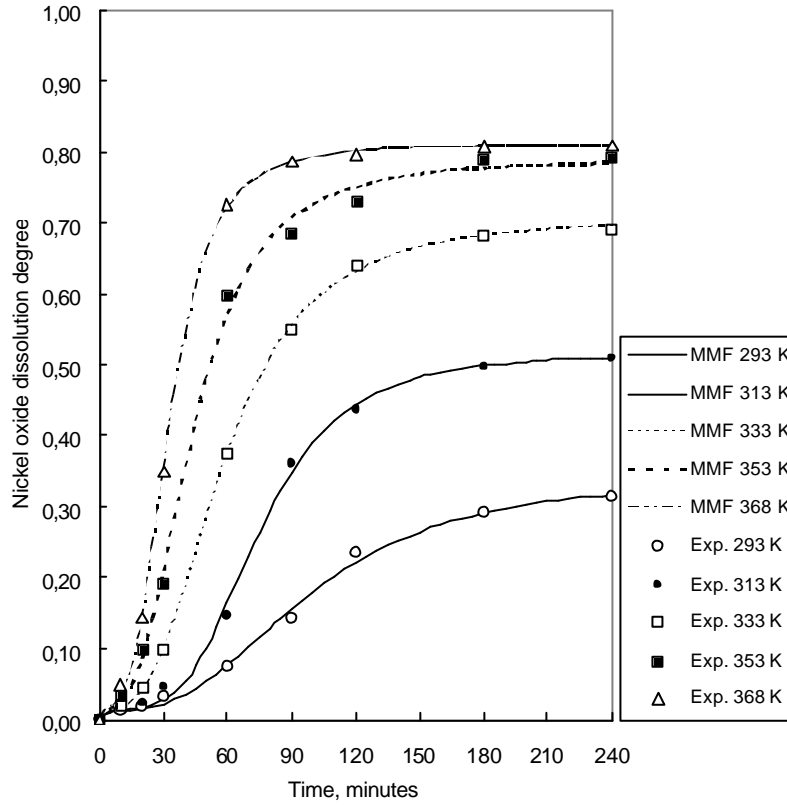


Fig. 2. Comparison between experimental data and MMF model

Using the MMF model, the time variation of  $\eta_{NiO}$  was determined, by the derivation upon time of the equation (3):

$$r_{NiO} = \frac{d\eta_{NiO}}{dt} = \frac{d}{dt} \left( \frac{a \cdot b + c \cdot t^d}{b + t^d} \right) = b \cdot (b - a) \cdot d \cdot \frac{t^{d-1}}{(b + t^d)^2} \quad (4)$$

Because  $b \gg a$ , we may admit that  $(b - a) \sim b$ , and equation (4) becomes:

$$r_{\text{NiO}} = \frac{dh_{\text{NiO}}}{dt} = b^2 \cdot d \cdot \frac{t^{d-1}}{(b+t^d)^2} \quad (5)$$

Based on equation (5),  $r_{\text{NiO}} = f(t)$  curves at different temperatures have been plotted (Figure 3).

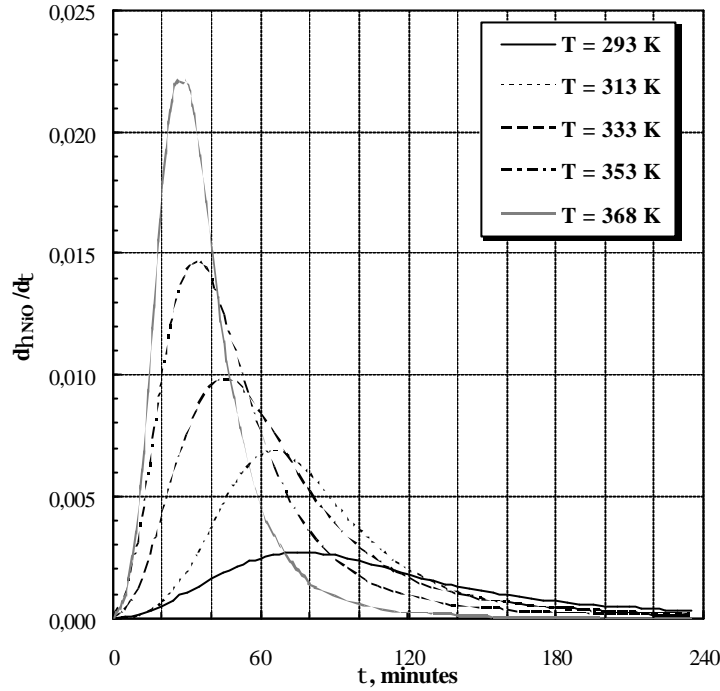


Figure 3. Derivated kinetic curves

As shown in fig. 3, the following observations can be mentioned:

- between 293 - 368 K, the 1<sup>st</sup> order derivatives of the kinetic curves reach a maximum value;
- the higher the temperature, the higher the maximum value of the kinetic curves' 1<sup>st</sup> order derivate;
- the higher the temperature, the shorter the time for reaching the maximum value of the kinetic curves' 1<sup>st</sup> order derivate.

An exponential correlation between the reaction rate of NiO,  $r_{\text{NiO}}$  (the 1<sup>st</sup> order derivate of the kinetic curve) and temperature can be obtained (Figure 4):

$$r_{\text{NiO}} = \frac{dh_{\text{NiO}}}{dt} = 2 \cdot 10^{-6} \cdot e^{0.0261T} \quad (6)$$

Also, a linear dependence between the reaction temperature and the time to reach the maximum value of  $r_{\text{NiO}}$  ( $t_{\text{max}}$ ) may be written as (Figure 5):

$$t_{\text{max}} = -0.6851 \cdot T + 276.45 \quad (7)$$

Based on the previous observations, we may assume that nickel dissolution from the catalytic structure is a complex process, formed by at least two steps:

- a first step, when reaction rate  $r_{\text{NiO}}$  increases from zero to a maximal value;
- a second step, when reaction rate  $r_{\text{NiO}}$  decreases from the maximal value to zero.

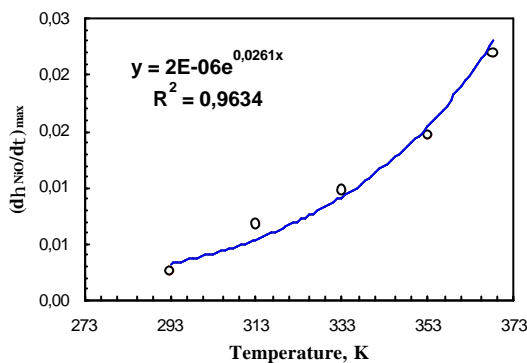


Fig. 4. NiO reaction rate maximum value vs. temperature

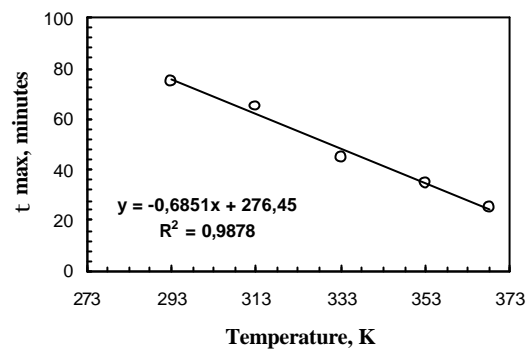


Fig. 5. Time to reach NiO reaction rate maximum value vs. temperature

As for pure NiO dissolution in sulfuric acid solutions there is no such behavior [21], we may charge this particular behavior to the form in which nickel is bonded in the catalyst's structure.

Literature data show a different reduction behavior of pure nickel oxide and Al<sub>2</sub>O<sub>3</sub> supported nickel oxide respectively [22 - 28]. Spectra of various NiO - Al<sub>2</sub>O<sub>3</sub> systems indicated that at least four different types of bonded nickel exist [32, 33]:

- I Ni<sup>2+</sup> ions in NiO network, fully reducible up to 673 K;
- II Ni<sup>2+</sup> ions in NiO network, partially reducible up to 673 K, fully reducible up to 1073 K;
- III Ni<sup>2+</sup> ions in the Al<sub>2</sub>O<sub>3</sub> network, irreducible up to 673 K, reducible up to 1073 K;
- IV Ni<sup>2+</sup> ions in the Al<sub>2</sub>O<sub>3</sub> network, hardly reducible (about 10%) up to 1073 K;

With respect to this classification, we can assume that the first step of the nickel dissolution, with increasing rate, is due to the nickel ions from the NiO network (I and II), and the second step of the nickel dissolution, with decreasing rate, is due to the nickel ions from the Al<sub>2</sub>O<sub>3</sub> network (III).

The first step of the nickel dissolution occurs fast and is independent of Al<sub>2</sub>O<sub>3</sub> dissolution. This step is evolving parallel with the dissolution of the reactive Al<sub>2</sub>O<sub>3</sub> forms, such as gamma-alumina.

The second nickel dissolution step is conditioned by the breaking of the alumina crystalline network. The dissolution rate of NiO decreases,  $\eta_{NiO}$  increases slowly, tending to a constant value. New quantities of nickel are dissolved as the reaction between Al<sub>2</sub>O<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> advances.

Even at high temperatures (353 - 368 K), and for a long reaction time (120 - 150 minutes), the dissolution degree of nickel remains steady, despite the fact that the solid structure still contains about 20% from the initial nickel quantity. This type of nickel (IV) is bond in extremely stable and hardly reactive spinellic combinations (i.e. NiAl<sub>2</sub>O<sub>4</sub>). To destroy them and to dissolute the spinellic nickel, high pressures and temperatures have to be applied to the catalyst - acid system [34 - 38].

## CONCLUSIONS

The kinetics of spent nickel based steam reforming catalysts acid leaching has been studied. The study allowed the elaboration of an empirical sigmoid model with four parameters that correlates best experimental data.

According to the proposed model, the nickel dissolution from NiO/a-Al<sub>2</sub>O<sub>3</sub> spent catalysts takes place in two steps: the fast dissolution of free Ni and NiO species - independent of Al<sub>2</sub>O<sub>3</sub> dissolution and the slow dissolution of NiO entrapped in the alumina network, strongly dependent of Al<sub>2</sub>O<sub>3</sub> dissolution.

For the second step of the leaching process, higher temperatures and longer reaction times are needed; despite this, spinellic nickel can be dissolved only at extreme temperatures and pressures.

## REFERENCES

1. \* \* \* Romanian patent RO-67180, **1979**;
2. \* \* \* Romanian patent RO-88269, **1985**;
3. Heves, A., Miclaus, C.: *Simpozionul national de ingineria proceselor chimice*, 4<sup>th</sup> ed., Piatra Neamt, 21-22 oct. **1988**, p. 167;
4. Potoroaca, M., Petrache, P.: *Simpozionul national de ingineria proceselor chimice*, 4<sup>th</sup> ed., Piatra Neamt, 21-22 oct. **1988**, p. 266;
5. \* \* \* Romanian patent RO-98337, **1990**;
6. \* \* \* Romanian patent RO-98332, **1990**;
7. \* \* \* US Patent 4,666,685, **1987**;
8. \* \* \* US Patent 4,670,229, **1987**;
9. \* \* \* *The Economics of Nickel*, 5<sup>th</sup> ed., Roskill Information Services Ltd., London, **1988**;
10. Wieworowski, E., Tinnin, R., Crnojevich, R.: A Cyclic Process for Recovery of Metals from Spent Catalysts, *1988 SME Annual Meeting*, Phoenix, Arizona, feb. **1988**, SME Reprint # 88-168;
11. LaRue, T.: AMAX Port Nickel – A New Dimension in Reclaiming Spent Catalysts, *1988 Spring AIChE National Meeting*, mar. **1988**;
12. \* \* \* *Nitrogen*, **1993**, 206, p. 49;
13. Case, A., Garretson, G., Wieworowski, E., *Ten Years of Catalyst Recycling; a Step to the Future*, **AMAX Metals Recovery Inc. & CRI-MET**, <http://www.cri-met.com/>, **1995**;
14. Gavrilă, L.: *Researches concerning the recovery of nickel from spent catalysts used in the chemical and petrochemical industry*, PhD Thesis, Technical University “Gh. Asachi” Iasi, **1999**;
15. Gavrilă, L., Zichil, V.: Désagrégation en milieu acide des catalyseurs usés de type NiO/a-Al<sub>2</sub>O<sub>3</sub> - 1. Modèles algébriques de bilan de matériaux, *Actes du Colloque Franco-Roumain de Chimie Appliquée*, (Fînaru, A., Azzouz, A., Gavrilă, L., Grandclaude, P. - eds), Ed. Alma Mater, Bacău, **2000**, p. 124 - 131;
16. Gavrilă, L., Asaftei, S., Ivascan, S.: Capitalization possibilities of spent catalysts with low nickel content, *Conferinta de Chimie si Inginerie Chimica*, “Politehnica” University Bucharest, vol. 1-I, **1995**, p. 230-235;

17. Gavrilă, L., Ivascan, S., Tudorache, E., Asaftei, S.: Valorificarea catalizatorilor uzati cu continut de nichel din industria amoniacului - 1. Cercetari privind posibilitatile de solubilizare a nichelului, *Revista de chimie* (Bucharest), **47** (11), p. 1039 - 1045;
18. Gavrilă, L., Istrati, L., Simion, A.I.: Valorisation des catalyseurs uses de type NiO/a-Al<sub>2</sub>O<sub>3</sub> - 3. Cinétique de la solubilisation de l'oxyde de nickel, *Actes du Deuxième Colloque Franco-Roumain de Chimie Appliquée*, (Gavrilă, L., Fînar, A., Grandclaude, P. - eds), Ed. Alma Mater, Bacău & Tehnica Info, Chisinau, **2002**, p. 281 - 284;
19. Gavrilă, L., Zichil, V.: Désagrégation en milieu acide des catalyseurs uses de type NiO/a-Al<sub>2</sub>O<sub>3</sub> - 2. Modèles cinétiques et mathématiques, *Actes du Colloque Franco-Roumain de Chimie Appliquée*, (Fînar, A., Azzouz, A., Gavrilă, L., Grandclaude, P. - eds), Ed. Alma Mater, Bacău, **2000**, p. 132 - 140;
20. Hyams, D., *CurveExpert®*, Version 1.31, **1996**;
21. Chirulescu, T., Ciobanu, C., Serban, Gh., *Revue Roumaine de Chimie*, **17** (9), **1972**, p. 1509;
22. Trambouze, Y., *J. Chim. Phys.*, **47**, **1950**, p. 258;
23. Vigner, S., Jeannot, F., *Gas* (Roma), **15** (11), **1965**, p. 340;
24. Hagigara, H., *Bull. Chem. Soc. Japan*, **38** (12), **1965**, p. 2163;
25. Takamura, Y., Morita, Y., Yamamoto, K., *Bull. Japan Petrol. Inst.*, **9**, **1967**, p. 13;
26. Pospisil, M., Cabica, L., *Coll. Czech. Chem. Comm.*, **35** (5), **1970**, p. 1319;
27. Bousquet, J.L., Dalmai, G., Imelik, G., Leclercq, C., *J. Microscopy* (Paris), **9** (3), **1970**, p. 301;
28. Roman, A., Delmon, B., *J. Catalysis*, **30**, **1973**, p. 333;
29. Shirokov, Yu., G., *Zh. Prikl. Khim.*, **46** (2), **1973**, p. 287;
30. Ivana, E., Bejan, L., Moldoveanu, I., Georgescu, N., Crisan, D., Bucur, I., *Revista de Chimie* (Bucharest), **34** (10), **1983**, p. 887;
31. Wilde, M., Kraft, M., Schödel, R., Kraak, P., *Chem. Techn.* (Leipzig), **39** (5), **1984**, p. 214;
32. Marchidan, R., Butucelea, A., Craiu, M., Manaila, R., Trutia, A., *Revista de Chimie* (Bucharest), **38** (1), **1987**, p. 57;
33. Craiu, M., Marchidan, R. si Stanica, N., *Revista de Chimie* (Bucharest), **38** (11), **1987**, p. 1007;
34. Manoliu, C., Zugravescu, P. Gh., *Dezagregarea sub presiune în chimia analitica*, Editura Tehnica, Bucuresti, **1988**;
35. \* \* \* Romanian Patent RO-70780, **1980**;
36. \* \* \* Romanian Patent RO-71156, **1982**;
37. \* \* \* Romanian Patent RO-83031, **1984**;
38. \* \* \* Romanian Patent RO-84612, **1984**;

---

Received: 12.15.2002