Formation and application of hydrogen in non-ferrous metallurgy

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Abstract:

Introduction/purpose: Hydrogen is the most abundant element in the universe (75 % by mass) and the lightest element (with a density of 0.00082 g/cm^3) which consists of only one proton and one electron. Because of its presence in many different forms such as gaseous hydrogen, its plasma species, water, acid, alkalline, ammmonia and hydrocarbons, it has various applications in different industrial disciplines.

Methods: Different hydrometallurgical and pyrometallurgical methods are considered in order to point out many different processes such as formation of hydrogen, reduction of metallic oxides and chlorides, and electrochemical reactions such as hydrogen overvoltage and the spillover effect. Ultrasonic spray pyrolysis enables the formation of very fine aerosols which can be used for the production of metallic powders.

Results: Hydrogen formation was observed during the dissolution of metallic allloys with hydrochloric acid. The reduction of metallic oxides and metallic chlorides by hydrogen leads to the formation of metallic powders. Metallic powders were collected by a new developed electrostatic precipitator.

Conclusion: Hydrogen can be applied in different reduction processes for the production of metallic powders. Recycling processes can be used for the formation of hydrogen. A new research strategy for powder production is proposed combining recycling of the black mass of used Li-Ion batteries, ultrasonic spray pyrolysis, and hydrogen reduction.

Key words: hydrogen, reduction, formation, acid, recycling, electrostatic precipitator.

Introduction

Hydrogen as the key element in energy transition replacing fossil fuels and their CO_2 emissions was used as a reducing agent instead of carbon thus attracting strong interest in hydrometallurgy and pyrometallurgy of non-ferrous metals (Stopić et al, 1997b). Control of hydrogen formation during hydrometallurgical processes such as electrocoagulation and winning electroysis has a high significance for metal recovery (Rodriguez et al, 2007b)

During sulphuric acid pressure leaching of copper oxidic ores containing silicates, the leaching solution contains copper sulfate with a low concentration of copper (approx. 5-10 g/L). After solvent extraction, the concentration of copper is increased until 30-40 g/l. Copper formation is possible by using hydrogen reduction in an autoclave under increased temperature (Hage et al, 1999). One version of this reduction process is gaseous reduction where metals are precipitated from leach solutions by direct contacting with reducing gases such as hydrogen and carbon monoxide. For the same fuel consumption, hydrogen reduction has the potential to produce two to six times as much metal as the competing traditional electrowinning process (Sista & Sliepcevich, 1981). To date, gaseous reduction has been practiced commercially primarily in batch operations or in semi-continuous, stirred autoclaves and tubular reactors. Under high pressure and temperature conditions, hydrogen reduction of aqueous copper sulfate in a continuous flow tubular reactor requires strict control of both feed temperature precipitation of basic copper sulfate and inlet pH-values (about pH-Value of 1.8) to prevent the formation of cuprous oxide during reduction. A bench scale investigation on the hydrogen reduction of a highly acidic copper bleed solution was performed in a titanium lined autoclave of 1 L. A producing 99% copper powder recovery which was reached at a pressure of about 2400 kPa, a reaction temperature of 453 K, and a stirring speed of 400 rpm for a reaction time of 2 h (Agrawal et al, 2006).

Similarly to copper production, an alternative process to electrowinning for the recovery of nickel from purified nickel solutions is hydrogen reduction under high pressure and high temperature conditions (Crundwell et al, 2011). Hydrogen reduction is carried out by injecting hydrogen into aqueous ammoniacal nickel sulfate solutions in stirred high-pressure autoclaves. The following steps are performed: the preparation of nickel ‘seed’ powder; the reduction of solution batches; the finishing of a 50 tonne “lot” of nickel powder; and the preparation of the autoclave for a new cycle.

This literature review aims at advances in understanding the role of hydrogen in non-ferrous metallurgy. The formation of hydrogen and its application for the synthesis of metallic powder will be explained in this study.

Hydrogen formation in hydrometallurgical processes

The formation of hydrogen was presented in zinc winning electrolysis, the treatment of wastewater with copper electrolysis, and in the treatment of black mass for recycling used Li-Ion batteries.

Zinc winning electrolysis

The formation of hydrogen in zinc winning electrolysis was performed in an electrolytic cell from the water solution of zinc sulfate, as shown in Figure 1.

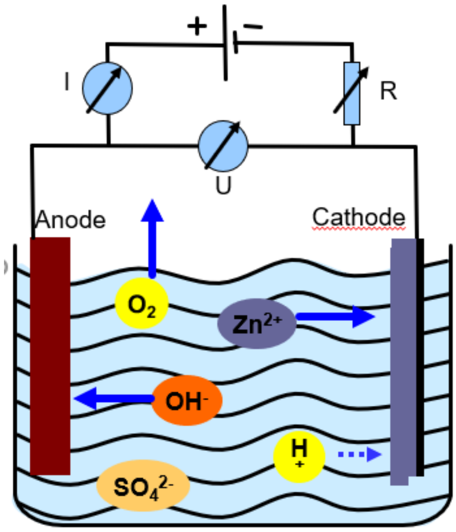

Figure 1 – Electrolytic cell
Рис. 1 – Электролизная ячейка
Слика 1 – Ћелија за електролизу

The formation of hydrogen is described via the following chemical reactions:

At the cathode:

$Zn^{2+} + 2e^{-} \rightarrow Zn^{0}$ (1)

At the anode:

$H_2O \rightarrow {}^{1}/_{2}\, O_2 + 2\, H^{+} + 2e^{-}$ (2)

Under the standard conditions, hydrogen is more noble than zinc and therefore zinc cannot be precipitated in the electrolysis of aqueous solutions. Every electrochemical reaction is inhibited in a different way for hydrogen, as shown in Figure 2.

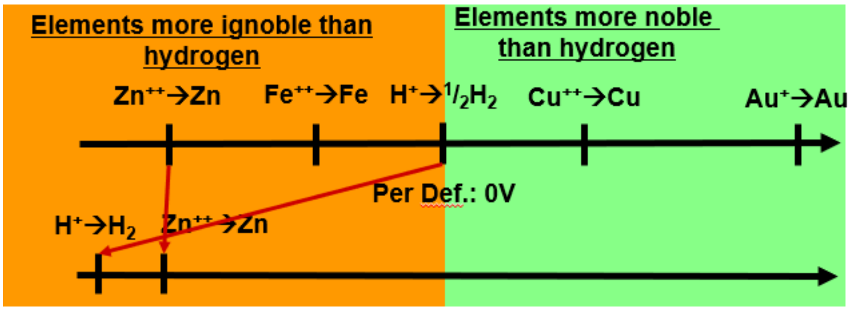

Figure 2 – Hydrogen overvoltage in zinc winning electrolysis
Рис. 2 – Перенапряжение водорода при получении цинка электролизом
Слика 2 – Пренапетост водоника у добијању цинка електролизом

The movement of the potential is enabled through the choice of different parameters: concentration of sulfuric acid, electrolyte temperature in an electrolytic cell, current density, and concentration of zinc in an acidic solution. Therefore, hydrogen overvoltage (potential difference that can be found between an electrode and a reversible hydrogen electrode within a single solution) leads to zinc precipitation as shown in Figure 2. Hydrogen is formed at an increased temperature of electrolytes (60°C), smaller concentration of zinc in an acidic solution, smaller current density and in the presence of iron and copper ions (catalytic effects). The analysis of the mechanism and kinetics of the hydrogen evolution reaction has confirmed that the hydrogen evolution reaction (HER) is the simplest electrocatalytic reaction (Lacia, 2019). With the development of renewable energy sources, electrolytic production of hydrogen becomes an alternative way of hydrogen production for internal combustion engines and fuel cells.

Electrocoagulation method for hydrogen formation

Electrocoagulation (EC) is an old electrochemical technique for treating polluted water using electricity instead of expensive chemical reagents such as sodium hydroxide needed for a chemical precipitation. EC was firstly proposed in London in 1889, where a sewage treatment plant was built and an electrochemical treatment was used via mixing domestic wastewater with saline. In the United States, J.T. Harries patented a wastewater treatment by electrolysis using sacrificial aluminium and iron anodes in 1909. Electrocoagulation (EC) may be a potential answer to environmental problems dealing with water reuse, hydrogen production, and rational waste management. The Integrated Treatment of Industrial Wastes towards Prevention of Regional Water Resources Contamination (INTREAT) Project results (2004-2006) confirmed the feasibility of the EC process for industrial contaminated effluents from Cu production, taking into consideration technical and economical factors. (Rodriguez et al, 2007a). The EC-reactor uses electrodes from aluminium and iron. This EC-reactor is connected with the control unit as shown in Figure 3.

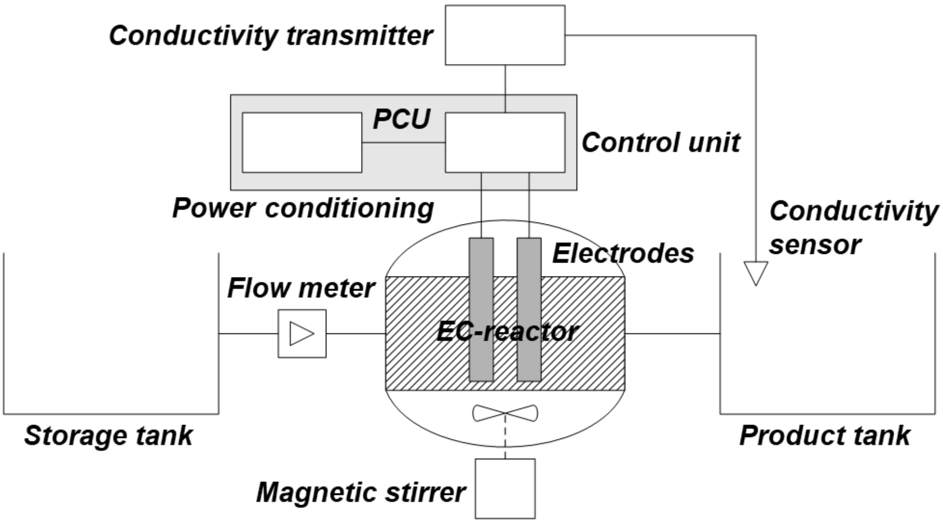

Figure 3 – Experimental setup for wastewater treatment by the EC-process
Рис. 3 – Экспериментальная установка для очистки сточных вод методом электрокоагуляции.
Слика 3 – Апаратура коришћена за пречишћавање отпадних вода процесом електрокоагулације

This EC-equipment enables the wastewater treatment and measurement of removed metals as well as the analysis of the concentration of the formed hydrogen.

As a working hypothesis, $Al^{3+(}$aq) ions are formed in the first step (Eq. 3).

$$Al(s) + 6H_2O \rightarrow Al(H_2O)_6^{3+} + 3e- \qquad (3)$$

At the cathode, hydrogen is evolved with the formation of OH^- (Eq. 4) thus raising the pH of the solution.

$$2H_2O + 2\ e- \rightarrow 2\ OH- + H_2 \quad (4)$$

This leads to the hydrolysis and condensation of $Al(H_2O)_6^{3+}$ in a stepwise fashion (Eq. 5) through $Al_2(OH)_2(H_2O)_8{}^{4+}$ leading finally to an amorphous insoluble polymeric hydroxide $[Al(OH)_3]n\ ^{\cdot}(H_2O)_x$

$$2\ Al(H_2O)_6^{3+} \rightarrow Al_2(OH)_2(H_2O)_8^{4+} + 2\ H_3O^+ \quad (5)$$

Hydrogen was formed during the decomposition of water and the transformation of complex aluminium hydroxide complexes to hydrogen ions.

Recycling the black mass from used Li-Ion batteries

Today, the production of Li-ion batteries is widely considered to be crucial technology since it can help decarbonize transport and increase the penetration levels of intermittent renewable energy sources.

Because of high demands, used lithium-ion batteries from different sources and chemistries (lithium cobalt oxide – LCO, and lithium nickel manganese cobalt oxide – NMC) were used after a vacuum chamber treatment, mechanical and thermal treatment by pyrolysis in the nitrogen atmosphere.

After that, thermally treated cells were submitted to shredding and magnetic separation to remove the steel casing from the cells and the Fe-rich fraction (Vieceli et al, 2023).

Subsequently, the black mass was sieved at 1 mm. The fraction rich in Al and Cu foils was removed in the coarse fraction (>1 mm) and the black mass was used for leaching with hydrochloric acid.

The main components of the black mass are graphite, mixed alloys (MnNi,MnNiCu and CoNi), oxides (CoO, NiO, $LiMnNiO_2$, $LiCoO_2$; $Mn_{0.8}Fe_{0.2}O_2$), carbonates (Li_2CO_3), fluorides (LiF), and phosphates ($LiCo(PO_4)_2$).

The leaching concentration of 4 mol/L was used in 100 L reactors (as shown in Figure 4), using a solid/liquid ratio of 0.3, at an atmospheric pressure, and at temperatures below 100°C.

The chemical composition of the black mass is shown in Table 1.

Table 1 – Chemical composition of the black mass from used Li-Ion batteries
Таблица 1 – Химический состав черной массы из использованных литий-ионных аккумуляторов
Табела 1 – Хемијски састав „црног праха" из отпадне Li-Ion батерије

Element	C	Li	Co	Mn	Fe	Cu	Ni	Al	total
(%)	31.5	3.42	15.5	9.24	0.74	7.92	6.73	5.00	79,85

Hydrogen was formed using the following reactions:

$$MnNi + 4\,HCl = MnCl_2 + NiCl_2 + 2\,H_2 \quad (6)$$

$$CoNi + 4\,HCl = CoCl_2 + NiCl_2 + 2\,H_2 \quad (7)$$

$$MnNiCu + 6\,HCl = CuCl_2 + NiCl_2 + MnCl_2 + 3\,H_2 \quad (8)$$

During this treatment of the black mass with hydrochloric acid, very hazardous hydrogen fluoride was formed:

$$LiF + HCl = HF + LiCl \quad (9)$$

Figure 4 –Reactors for the dissolution of the black mass from used Li-ion batteries
Рис. 4 – Реакторы для переработки черной массы из использованных литий-ионных аккумуляторов
Слика 4 – Реактори за растварање црне масе из отпадних Li-ion батерија

The formed hydrogen was observed in the reactors and its concentration measured using TESTO-devices for the gas analysis.

Application of hydrogen in the production of metallic powders

The application of gaseous hydrogen for the reduction of metallic oxides and metallic chlorides, in comparison to alternative reducing agents such as carbon and carbon monoxide, has some advantages, as shown with equations:

$$MeO + H_2 = Me + H_2O \quad (10)$$

$$MeO + C = Me + CO \quad (11)$$

$$MeO + CO = Me + CO_2 \quad (12)$$

$$MeCl_2 + H_2 = Me + 2\,HCl \quad (13)$$

$$2MeCl_2 + 2\,C = 2\,Me + CCl4 \quad (13)$$

The advantages of hydrogen as a reducing agent:

1. Formation of water instead of carbon monoxide and carbon dioxide through the reduction of metallic oxides,
2. Formation of an acid instead of hazardous carbon tetrachloride through a reduction of metallic chloride, and
3. Environmentally friendly process.

Hydrogen is used to be not only a source of clean fuel energy, but also a reducing agent for metals production in the current industrial decarbonization effort. Hydrogen is only commercially utilized in the production of a limited number of refractory metals (i.e., W, Mo) and partly utilized in Ni and Co metals production. An improvement of hydrogen reduction was obtained using the hydrogen spillover effect. The hydrogen spillover effect (HSPE) is the most important interfacial phenomenon in which active hydrogen atoms generated via the dissociation of H_2 on one phase (metal surface) migrate to other phases (support surface) and participate in the catalytic reaction of the substance adsorbed on that site (Shen et al, 2022).

The hydrogen spillover effect was confirmed for hydrogen reduction of nickel chloride and nickel oxides in the presence of palladium, copper and nickel (Stopić et al, 1997a). Hydrogen is mostly used for the synthesis of metallic powders from water solutions of metallic nitrates and metallic chloride by ultrasonic spray pyrolysis and subsequent hydrogen reduction (Gürmen et al, 2009). The equipment for the synthesis of metallic powder contains an ultrasonic generator, a furnace and an electrostatic precipitator, as shown in Figure 5.

Figure 5 – Ultrasonic spray pyrolysis equipment
Рис. 5 – Устройство для пиролиза ультразвуковым распылением
Слика 5 – Апаратура за распршивање водених раствора у ултразвучном пољу

Hydrogen is mostly used with argon in order to prevent the formation of an explosive mixture and to avoid the formation of ammonia. Concerning the applied flow rate of hydrogen and argon, the production rate amounts to about 5g of metal per one hour in laboratory conditions.

Metallic powder was usually collected with a wet scrubber or an electrostatic filter. The newest developed electrostatic precipitator by PRIZMA, Kragujevac, is shown in Figure 6.

Figure 6 – Electrostatic precipitator for collecting powder developed by PRIZMA, Kragujevac, Serbia
Рис. 6 – Электрофильтр для извлечения порошка, разработанный компанией PRIZMA, Крагуевац, Сербия
Слика 6 – Електростатички преципитатор за сакупљање прахова развијен у компанији „Призма”, Крагујевац, Србија

A new electrostatic precipitator uses a rotating electrode enabling the collection of powders avoiding condensation until 300°C.

Conclusion

Hydrogen is mostly formed during the zinc winning electrolysis, the electrocoagulation process, and through the recycling process using acid dissolving metallic alloys. The formed hydrogen is measured and stored in metallic powders such as LaNi5 in order to be used for the reduction process. As a favorable reducing agent in comparison to carbon and carbon monoxide, hydrogen is used for the formation of metallic powders. The ultrasonic spray pyrolysis of the water sollution of metallic chlorides and metallic nitrates, with subsequent hydrogen reduction, produces submicron and nanosized powders. The combined strategy of hydrogen formation and its application is shown in Figure 7.

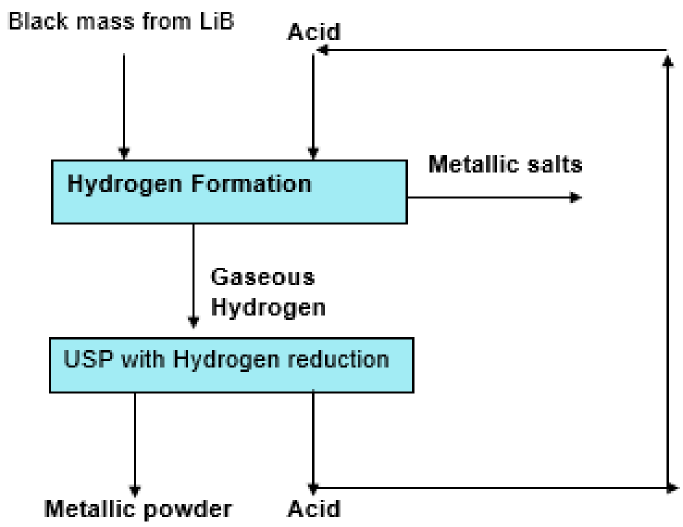

Figure 7 – Formation of gaseous hydrogen and its application
Рис. 7 – Образование газообразного водорода и его применение
Слика 7 – Формирање гасовитог водоника и његова примена

As shown in this figure, it is possible to recycle used acid and return it to the dissolution of black mass, which is an innovative route.

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Образование и применение водорода в металлургии цветных металлов

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РУБРИКА ГРНТИ: 61.13.21 Химические процессы
ВИД СТАТЬИ: обзорная статья

Резюме:

Введение/цель: Водород является самым распространенным элементом во Вселенной (75 % по массе) и самым легким *элементом (с плотностью 0,00082 г/см^3). Он состоит всего лишь из одного протона и одного электрона. Благодаря его содержанию во множестве различных форм, таких как газообразный водород и его плазменные разновидности, вода, кислота, щелочь, аммоний и углеводороды, он широко применяется в различных отраслях промышленности.*

Методы: В статье рассматриваются различные гидрометаллургические и пирометаллургические методы с целью выявления множества различных процессов, таких как образование водорода, восстановление оксидов и хлоридов металлов, а также электрохимические реакции, такие как перенапряжение водорода и побочные эффекты. Пиролиз ультразвуковым распылением позволяет получать мельчайшие аэрозоли, которые могут быть использованы для производства металлических порошков.

Результаты: При растворении металлических сплавов соляной кислотой выявлено образование водорода. Восстановление металлов из оксидов и хлоридов водородом приводит к образованию металлических порошков. С помощью нового разработанного электрофильтра были извлечены порошки металлов.

Выводы: Процессы рециркуляции могут быть использованы в производстве водорода. В свою очередь, водород можно использовать в различных процессах восстановления в производстве металлических порошков. В статье предлагается новая исследовательская стратегия, сочетающая производство водорода в процессе переработки «черной массы» из литий-ионных аккумуляторов с ультразвуковым напылением, термическим разложением капли и восстановлением водорода.

Ключевые слова: водород, восстановление, образование, кислота, рециркуляция, электрофильтр.

Формирање и примена водоника у металургији обојених метала

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ОБЛАСТ: хемијске технологије
КАТЕГОРИЈА (ТИП) ЧЛАНКА: прегледни рад

Сажетак:

Увод/циљ: Водоник је најраспрострањенији елемент универзума (75 % масених процената), као и најлакши (густина 0.00082 г/цм$^{3)}$), који *се састоји од једног протона и једног електрона. Због великог присуства у различитим формама, као што су гасовити водоник, плазма-облици, вода, киселина, базе, амонијак и једињења са угљеником, водоник има високу примену у многим индустријским дисциплинама.*

Методе: Различите приометалуршке и хидрометалуршке методе размотрене су у намери да истакну много различитих процеса – формирање водоника, редукција металних оксида и хлорида, као и електрохемијске реакције, као што је пренапетост водоника. Ултразвучно распршивање са термичким разлагањем капи омогућава формирање финих аеросола, који касније могу бити коришћени за производњу металних прахова.

Резултати: Водоник је формиран растварањем легура из „црне масе” добијене третманом отпадних литијум-јон батерија. Редукцијом металних оксида и металних хлорида водоником долази до формирања металних прахова. Они су сакупљани у новом ултразвучном преципитатору.

Закључак: Процеси рециклирања могли би бити искоришћени за формирање водоника који може бити примењен у различитим редукционим процесима за производњу металних прахова. Нова истраживачка стратегија комбинује производњу водоника у процесу рециклирања „црне масе” из литијум-јон батерија заједно са ултразвучним распршивањем, термичким разлагањем капи и водоничном редукцијом.

Кључне речи: водоник, редукција, формирање, киселина, рециклирање.

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