

ALUMINUM AND MAGNESIUM PRODUCTION - CHANGES AND PERSPECTIVES

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Abstract

Aluminum and magnesium are young metals in comparison to lead or iron but today commonly used. Their production is constantly growing. This is due to their universal application, eg. in aircraft industry, automotive industry, pharmaceuticals, electric and engineering industry, packaging. To the main producers of these metals belong: China, Russia, Canada and Israel. The amount of aluminum and magnesium production in the last 24 years has been presented also considering the changes that occurred in the main producers. The changes of magnesium production from electrolytic method to silicothermic reduction (e.g. Pidgeon method) have also been shown. Basic information concerning obtaining aluminum from ores by the Bayern method and electrolysis of alumina as well as receiving it from scrap via recycling has been given. The essential dangers for the environment have been pointed out as well as the perspectives of further aluminum and magnesium production.

Keywords: Magnesium, aluminum, production, electrolysis, recovery

1. INTRODUCTION

Magnesium was discovered in 1806 by Henry Davy, whereas aluminum in 1825 by Hans Christian Oersted. In 1884 the production of aluminum was about 60 kg, and its price circa 32 US\$ for 1 kg (it is worth mentioning that in 1852 the price was considerably higher - 1,200 US\$ for 1 kg) [1, 2]. Today the price of aluminum is about 1.2 US\$ for 1 kg and the production of primary aluminum (see **Table 1**) is almost 1,000,000 times bigger than in 1884 [3, 4]. Magnesium became a strategic material during the Second World War (in 1938 the production of magnesium was 33,500 tones, whereas five years later this production was about 12.7 times more (426,000 tones) [5]). Today the production is even twice as big as in 1943. It is not such a significant jump as in the case of aluminum, but data from **Table 2** shows that there is still a constant increase in the production of this metal [6, 7].

Table 1 Production of primary aluminum [3, 4]

Year	1900	2000	2010	2011	2012	2013	2014	2015
Al production in millions tones	19.30	24.00	41.80	44.90	46.10	47.80	50.50	58.30

Table 2 Production of magnesium [6, 7]

Year	1990	2000	2010	2011	2012	2013	2014	2015
Mg production in tones	354000	428000	737000	766000	795000	873000	973000	910000

The increasing production of such metals comes from their constant demand and universal application. Aluminum finds application almost in every part of our life (**Table 3**); it is known as domestic appliances (foil) as well as an excellent material for space shuttle. Magnesium, however, is not produced in such amount, but is almost applied in the same branches of industry like aluminum (automotive, electronic, airplanes, sport and marital - see **Table 3**). Additionally, it is the lightest metal used for every kind of construction; its small density enables to reduce the mass of the produced elements and as a result to reduce the cost of production. Wider

application is explained by the fact that it is universal and perfect material especially when the low mass is needed together with the high durability; even though the metal is harder to cast than zinc or aluminum. While, the application of magnesium and aluminum is still increasing; the economical, technological and ecological background of these metals production has changed.

Table 3 Aluminum and magnesium application [8-10]

Industry	Magnesium	Aluminum
automotive	many car producers such as Audi, Ford, Jaguar, Fiat replace steel and aluminum elements by magnesium - reduction of car mass about 100 kg causes lower fuel consumption (0.4 dm ³ per 100 km)	a modern car with elements made of aluminum can be 24% lighter than a car with components made of steel - this causes lower fuel consumption (2 dm ³ per 100 km);
airplanes	Mg is used in reverse thrust of airplanes like Boeing 737, 747, 757, 767 also in engines and turbines	2xxx, 3xxx, 5xxx, 6xxx, and 7xxx series of Al alloys are widely used in airplanes
electronic	many Mg alloys replace plastic elements - they have almost the same lightness, and additionally they are more resistant and durable; it is possible to obtain cast with very thin walls (eg. laptops, cellular phones, thermovisual cameras, telecommunication equipment)	production of electrical equipment (e.g. about 25 % of Al produced in Russia is used for that purpose); it is the most efficient way of transmitting electric power (e.g. wires for high-voltage power lines and cables)
medical	Mg is used as a material for implants - its alloys density (1.7-2.0 g/cm ³) is similar to bone density (1.8-2.1 g/cm ³); Mg implants are nontoxic, have good biological compatibility and undergo biodegradation	aluminum salts are used to reinforce vaccines; aluminum hydroxide is required to cure peptic ulcer disease, dyspepsia, and gastric irritation; Al is added to deodorants and anti-perspirants
constructions	components made from magnesium: door handles, locks, bolts, lock casings, profiles connectors, decorative accessories, interior fittings; magnesium is applied for the tools in construction works, e.g.: chain saw, shears, driller machine, nailing machine	20 % of Al production: ceilings, walls, window frames, blinds, doors, stairs, roof covers, wall panels partitions, HVAC systems; to construct houses, shopping centers, stadiums, bridges; to restore and reconstruct historical buildings
other	steel desulphurization; modification of cast iron, electrochemical industry (anodes); reducing agent for metals such as: Be, Zr, Hf, U; alloying elements in Al alloys, sport equipment e.g. club, bow, skate	irrigation systems, elements of propulsion plants of manufacturing equipment, conveyor belts and automated control systems, stairs, scaffolds and fittings, foils

2. CHANGES IN MAGNESIUM PRODUCTION

To 1990 such countries like: USA, USSR, Norway, Canada and France belonged to the main producers of magnesium (**Figure 1**). From the year 2000 the dominant producer of magnesium has been China - the production of magnesium in this country between years 2000-2010 tripled, mainly because of high costs of the process in Canada, France or Norway. Most of the magnesium plants in those countries were closed due to the lack of competitiveness. Today, magnesium is produced in small amount only in those countries, which have easy access to the cheap minerals containing magnesium (eg. Israel - its technology is based on water and carnalite from the Dead Sea). **Table 4** presents available methods of magnesium production.

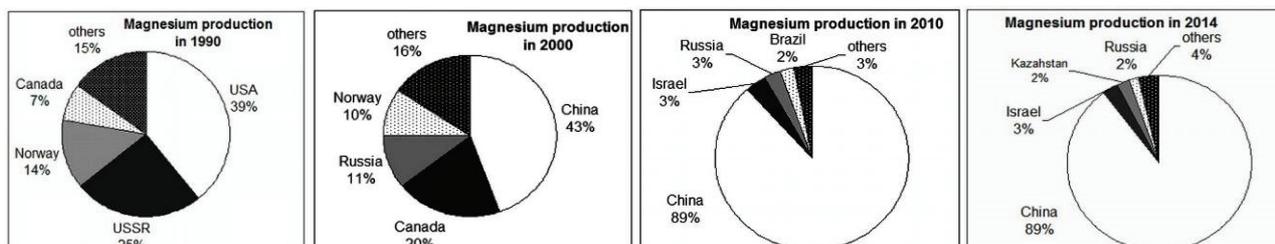


Figure 1 Magnesium main producers in years: 1990, 2000, 2010 and 2014 [6, 7]

Table 4 Methods of magnesium production [11-16]

Parameters	Methods of obtaining
Electrolytic methods	
Steps of obtaining	Obtaining the magnesium chloride from different materials such as: <ul style="list-style-type: none"> by-products from potassium production or solution of Mg minerals in HCl (Norsk Hydro process), brines containing 33-34 % of MgCl₂, they are concentrated by evaporation using solar energy (National Lead process) or using conventional dehydration process (Dow Chemical process), oxides compounds such as MgO or MgCO₃ - chloride roasting (MagCan, Alberta, Canada or IG Farben, Norsk Hydro, Norway), synthetic carnalite (30-34 % MgCl₂, 21-25 % KCl, 3.5-9 % NaCl and up to 2 % CaCl₂) - Russia, natural carnalite - Dead Sea Magnesium Work (DSM), Israel, serpentinite coming from the residual of asbestos production (Magnola process). Dehydration of the obtained magnesium chloride: <ul style="list-style-type: none"> in the temperature 820 K in the atmosphere of chlorine or anhydrous chloric acid (Norsk Hydro), replacing water by ammonia (CSIRO, Alcan), reduction of activity of magnesium chloride (VAMI, Magnola), reduction by chlorine at the presence of carbon (USMAG). Dehydration of carnalite is easier than obtaining magnesium chloride from brines and is conducted in two stages: dehydration of carnalite KCl·MgCl ₂ ·6H ₂ O to KCl·MgCl ₂ ·2H ₂ O in fluidized-bed furnace (573 K), dehydration of KCl·MgCl ₂ ·2H ₂ O to anhydrous carnalite KCl·MgCl ₂ in chlorinator (1023 K).
Working plant/ their production	Dead Sea Works Ltd. (VAMI/UTI), 27,500 Mg/year; AusMagCorp, Queensland, Australia (Alcan), 1,500 Mg/year; Ust Kamenogorsk Works, Kazakhstan, 50,000 Mg/year; Solikamsk Magnesium Work, Russia (VAMI), 20,000 Mg/year; VSMPO - Avisma Corp., Berezniki, Russia (VAMI), 55,000 Mg/year
Solid Oxide Membrane Method (SOM)	One of the alternative for electrolysis method; it is based on electrolysis of magnesium oxide melted in solution of fluoride salts (MgF ₂ ·CaF ₂ ·MgO); temperature 1423-1573 K; magnesium oxide dissociate to the magnesium and oxygen; gaseous magnesium is placed on cathode, and then condensated in the appropriate aggregates; reaction can be written in the following form: Mg ²⁺ + C + O ²⁻ = Mg _(g) + CO _(g)
Thermal methods	
Pidgeon method	The steps of the process are following: <ul style="list-style-type: none"> preparing charge materials - production of ferrosilicone in arc furnace (1873 K) and calcination of dolomite (1273-1573 K): $\text{CaMg}(\text{CO}_2)_3 = \text{CaO} + \text{MgO} + 2\text{CO}_2$ $\text{Fe}_2\text{O}_3 + 4\text{SiO}_2 + 11\text{C} = 2\text{FeSi} + 10\text{CO} + \text{SiC} + \text{SiO}$ mixing and reduction of charge materials in horizontal retorts made from heat-resisting (Fe-Ni) steel, head of the retort (condenser) is cooled by water, magnesium is set on condenser wall reduction of magnesium oxides: $2\text{MgO} + 2\text{CaO} + \text{FeSi} = 2\text{Mg} + \text{Ca}_2\text{SiO}_4 + \text{Fe}$ temperature: 1433 K, pressure: 13-67 Pa, energy consumption: 30 MWh, capacity: 70 kg/day melting, refining, casting
Bolzano	charge: dolomite and FeSi; temperature: 1473 K, pressure lower than 400 Pa
Magnetherm	charge: dolomite, bauxite, FeSi; temperature: 1800-1900 K, pressure: 40-67 Pa, the main reaction: $2\text{CaO} \cdot \text{MgO} + (x\text{Fe})\text{Si} + n\text{Al}_2\text{O}_3 = 2\text{CaO} \cdot \text{SiO}_2 \cdot n\text{Al}_2\text{O}_3 + 2\text{Mg} + x\text{Fe}$
Mintek	charge: dolomite, bauxite, FeSi, Al scrap; temperature: 1973 K, pressure: 86126 Pa, the main reaction: $2\text{CaO} \cdot \text{MgO} + (x\text{Fe})\text{Si} + n\text{Al}_2\text{O}_3 = 2\text{CaO} \cdot \text{SiO}_2 \cdot n\text{Al}_2\text{O}_3 + 2\text{Mg} + x\text{Fe}$ Mintek process has higher capacity than Magnetherm process - there is also no problem to keep vacuum as in Pidgeon or Magnetherm process, however, the purity of obtained magnesium is lower (97.7 %) than in Pidgeon method (99.75 %); so in Mintek process magnesium should be refined
Other methods	<ul style="list-style-type: none"> reduction by carbon - charge: magnesite, carbon → MgO + C = Mg_(g) + CO; temperature: 2073 K, normal pressure, disadvantage: reaction of Mg vapours and carbon monoxide when cooling reduction by aluminum - charge: dolomite, Al scrap → 4MgO + 2Al = 3Mg_(g) + MgAl₂O₄; temperature: 2073 K, normal pressure, disadvantage: needs a lot of energy
Working plant	75 % of whole silicothermic production in China is placed in Shanxi, Ningxia and Henan provinces (more than 120 plants); smaller plants are located in Shaanxi, Hebei, Liaoning and Jiangsu

Magnesium can be produced electrolytically or thermally. The first method is based on obtaining the anhydrous magnesium chloride from magnesite, salt water, brine or serpentinite and then conducting the electrolysis process. This method was commonly used in the years 1970-2000. Then, it was almost totally replaced by thermal technologies. Thermal method is based on the direct reduction of magnesium oxide by ferrosilicon - Pidgeon or Magnetherm method. It is also possible to apply carbon or magnesium as a reducing agent. Pidgeon process is really easy to maintain, does not need complicated apparatus, the production in this method is really easy to be accommodated to the specific demands and needs low investment cost comparing to the electrolytic process, e.g. for Australia Magnesium process, new one introduced in 2007-2008 based on electrolysis the investment cost was 10,000 USD per 1 tone of Mg whereas for Pidgeon process this cost is 3,000 USD per 1 tone of Mg [14].

3. CHANGES IN ALUMINUM PRODUCTION

The main producer of aluminum is also China (more than 100 aluminum plants), however it is not so dominant as in the magnesium production - only about 50 % of the whole primary production (see **Figure 2**). The second and third places take Russia and Canada respectively with 6 and 7%. 1990 leader - USA produces today only 3.5 % Al.

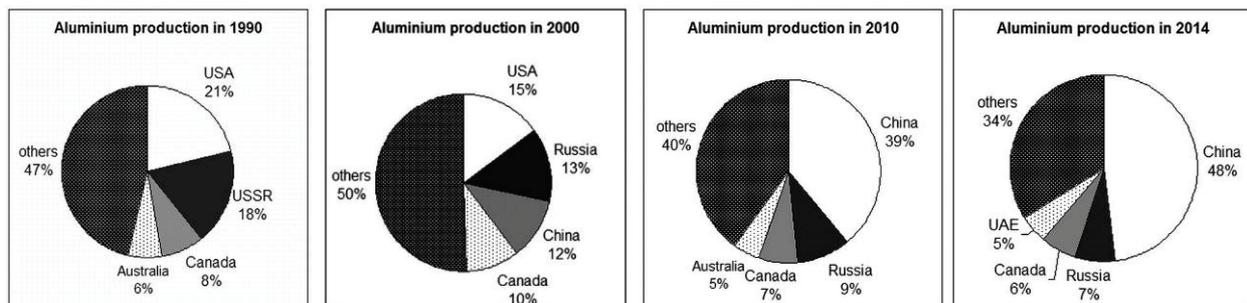


Figure 2 Main producers of primary aluminum in years: 1990, 2000, 2010 and 2014 [3, 4]

Today aluminum can be obtained in two ways. Primary aluminum (2/3 of whole aluminum) is produced from ores in two stages: the first one is an appropriate treatment of bauxite in order to obtain alumina; the second is the fused-salt electrolysis of obtained alumina dissolved in cryolite (see **Table 5**) [17-21]. This method is characterized by the low efficiency, high energy consumption and high toxicity of emitted fluorine compounds. Possibilities of further improvement of this method are rather limited; however there was a variety of changes and innovation in conducting this process. During the last fifty years there was a significant progress in electrolytic cells construction (see **Table 6**). Generally today electrolytic cells differ in size and anode construction. Today the Prebake technologies predominate because of their lower environmental impact (all new facilities built today using this technology). The secondary aluminum (1/3 of Al production) is obtained by scrap treatment. 1/5 of the aluminum scrap comes from packages, 2/5 from transport, whereas about 1/3 from building engineering [20].

4. PERSPECTIVES AND CONCLUSIONS

Magnesium is known as the material of the future. However, the Pidgeon method used for its production is, as mentioned above, easy to install and its maintenance has also some disadvantages. It uses a lot of natural resources (for 1 tone of Mg it is needed 11 tones of dolomite, 1.1 tones of ferrosilicon and 4.5 to 10 tones of carbon) and leads to serious environmental pollution. From all methods Pidgeon process is ecologically the worst, it is characterized by the highest emission of gases in the local scale (25 kg CO₂, 60 g CO, 68 g NO_x and 136 g SO₂ for 1 Mg tone [22]) and the GPW factor (see **Table 7**). Magnesium production in China belongs to the most environmentally polluted (90 % of whole GWP) comparing with other countries (GWP for Pidgeon

process is 8 times higher than for electrolytic methods). In China there are a lot of new plants using Pidgeon methods. The only alternative is recycling process; although it is not so widely implemented. Aluminum is a very young metal; however its production is really enormous and also problematic. During Bayern's method a lot of waste (red mud) is produced - per 1 tone of alumina 1 to 1.6 Mg of red mud. It is estimated that the amount of red mud formed annually in the world is bigger than 66 million tones [21]. The electrolytic process of alumina is energy-consuming (up to 30 % of total production costs). Today 60 % of energy supplied to aluminum industry comes from renewable natural resources (mainly water energy). During electrolysis a lot of harmful substances such as dusts, fluorine compounds and carbon derivatives are emitted to the environment. Alternative to such process is scrap recycling - 1 kg of secondary aluminum saves 4 kg of bauxite, 4 kg of chemical compounds, 14 kWh of energy and limit production of many waste; however it is not possible to produce more than 1/3 of total aluminum in that way because of its life cycle. Probably every man has some aluminum products, and in the nearest future nothing may change - the role of aluminum in economic development and civilization is still increasing.

Table 5 Methods of primary aluminum production [17-21]

Stages	Characteristics
Bayern method - there are many known methods of obtaining alumina from ores: Müller, Kuzniecowa-Inkowska, Bayern, Grzymek, Bretsznajder; however, today on a large scale 95 % of all bauxites are treated by Bayern method	
Digestion	grinded bauxite ores (in the form of gibbsite, boemite and diasporite plus 2-20 % SiO ₂ , Fe ₂ O ₃ and up to 10 % TiO ₂) are dissolved in caustic soda, pressure: 1.8-2.4 MPa, temperature: 400 K - 500 K, reaction: $Al_2O_3 \cdot 3H_2O + 2NaOH = 2NaAlO_2 + 4H_2O$; during digestion process red mud as a waste is formed - it is an insoluble mixture collected at the bottom of the autoclaves after dissolving bauxite in caustic soda, strongly alkaline (pH = 13), contains the following elements and compounds: silica, Al, Fe, Ca, Ti, Na, K, Cr, V, Nb, Ba, Mn, Cu, Pb, Zn and many others in trace concentration
Precipitation	NaAlO ₂ solution is cooled and then aluminum hydroxide precipitates in the solid form; the solution is usually seeded with fine crystallized gibbsite obtained from previous cycles, these crystallized seeds are filtrated from the solution and added in order to speed up the gibbsite crystallization; main reaction: $2H_2O + 2NaAlO_2 = Al_2O_3 \cdot H_2O + 2NaOH$; process temperature: 303 K
Calcination	aluminum hydroxide is then heated in the temperature 1370-1470 K in rotary kiln to decompose it to alumina (non-hygroscopic) and water, the following products are obtained: $Al_2O_3 \cdot 3H_2O \xrightarrow{(523\text{ K})} Al_2O_3 \cdot H_2O + 2H_2O \xrightarrow{(773\text{ K})} \gamma\text{-}Al_2O_3 + H_2O \xrightarrow{(1223\text{ K})} \alpha\text{-}Al_2O_3$
Electrolysis of alumina	
Parameters	temperature: 1223 K, current density: 0.75 A/cm ² , current efficiency: 95 %, working voltage: 4.0-4.5 V
Anodes	<ul style="list-style-type: none"> Söderberg smelters use a continuously created anodes made by the addition of pitch to the top of the electrolytic cell, the heat generated by the reduction process is used to bake the pitch into the carbon form required for the reaction with alumina; two types: Horizontal Söderberg Stud (HSS) and Vertical Söderberg Stud (VSS) depending on the current introduction to the cell, Prebake technology use anodes which are baked in large gas-fired ovens at high temperature before being lowered into the cell, they replace the consumed once; dominant technology; three different types: PFPB - point feeder, CWPB - central wall, SWPB - side wall, depending on the way the alumina is refilled in the cell, the most efficient is PFPB Reaction occurring at the anodes: $(Al_2O_2F_4)^{2-} + 4F^- + C = 2AlF_4^- + CO_2 + 4e^-$, $4F^- + C = CF_4 + 4e^-$
Cathodes	graphite bottom of the cell, the following reactions take place during the electrolysis process: $AlF_4^- + 3e^- = Al^0 + 4F^-$, $AlF_6^{3-} + 3e^- = Al^0 + 6F^-$, $Na^+ + F^- = NaF$
Electrolyte	anhydrous melted alumina Al ₂ O ₃ (8-10 %) in cryolite (Na ₃ AlF ₆) with density: 2.1 g/cm ³ , small amount of fluorides (MgF ₂ , CaF ₂) are added to decrease the temperature of electrolyte melting
Refining	the obtained aluminum consists of ≥ 99.7 % Al; 0.1±0.3 ppm H ₂ ; 30±150 ppm Na; 2±5 ppm Ca; 0±20 ppm Li; inclusions: oxides, borides, carbides e.g. Al ₄ C ₃ ; all aluminum should be refined to decrease the level of hydrogen below 0.1 ppm, refining process is conducted e.g. by blowing the melt by inert gas (argon), additionally if the inclusions should be also removed the filtration process is required; today it is possible to use one reactor for refining and filtering - refining reactor contains special kinds of filters

Table 6 Changes of the electrolytic cell parameters during the last sixty years [20]

Time	1955-1965	1980	today
Type of electrolytic cell	Central wall	Side wall	Point feeder
Current intensity (kA)	80-140	175-280	350
Current efficiency (%)	85-89	93-95	95
Energy consumption (kW·h ⁻¹)	15.2-17.0	12.9-13.2	12.3
Amount of work (hour/tonne Al)	10-15	3.5-5.8	2.5
Electrolytic cell work (hour)	26-30	65-85	85

Table 7 Comparison of global warming potential (GPW) for Mg, Al, Ti and steel [13, 14, 22]

Metal	steel	Al	Ti	Mg (Pidgeon)	Mg (AM)	Mg (Bolzano)	Mg (Magnetherm)
GPW (kg CO ₂ ·kg ⁻¹)	6.8	22.4	35.7	62.7	47.3	33.2	37.0

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