

MIROSLAV SOKIĆ  
VLADISLAV MATKOVIĆ  
BRANISLAV MARKOVIĆ  
ZVONKO GULIŠIJA  
ALEKSANDRA PATARIĆ  
MARIJA MIHAILOVIĆ  
ZORAN JANJUŠEVIĆ

Institute for Technology of Nuclear  
and Other Mineral Raw Materials,  
Belgrade, Serbia

SCIENTIFIC PAPER

UDC 546.41:552.541(497.11):66:544

DOI 10.2298/CICEQ120817022S

## THE POSSIBILITIES OF OBTAINING METALLIC CALCIUM FROM SERBIAN CARBONATE MINERAL RAW MATERIALS

### Article Highlights

- Defined technological scheme of the calcium production from Serbian limestones
- The influence of operating parameters on CaCO<sub>3</sub> calcination was examined
- The dissociation is completed in 15 min at 1200 °C
- The satisfactory rate for CaO aluminothermic reduction is accomplished at 1200 °C in 2 h
- The content of hardly evaporated metals in obtained Ca is very low

### Abstract

*We present experimental investigations that define both the technological scheme of calcium production from limestone by aluminothermic process and the basic operating parameters of the particular technological phases. The limestone with high content of Mg, Na and K was used in the study. X-ray analysis reveals that the samples contain mainly calcite with small amount of dolomite. At first, the effects of temperature, time and granulometry on the calcium carbonate calcination were examined. The dissociation process was completed in 10-15 min at 1200 °C, and the dissociation rate increased with decreasing particle size down to 5 mm. Afterwards, the aluminothermic reduction process of calcium oxide was investigated. At a temperature of 1200 °C and vacuum of at least 3 kPa, the reduction process completed within 2 h. The chemical composition of calcium oxide and calcium showed increased content of magnesium oxide and alkaline oxides (especially sodium).*

*Keywords: limestone, calcination, calcium oxide, aluminothermic, calcium.*

Pure calcium is a bright silvery-white metal, extremely soft and ductile. The metal oxidizes rapidly in the presence of moisture or in a dry air at temperature above 300 °C [1,2]. Calcium reacts readily with water, forming hydrated lime (calcium hydroxide) and hydrogen. It melts at 845 °C, boils at 1420 °C, and can be purified by distillation in an inert atmosphere or in a vacuum.

Owing to its chemical reactivity with oxygen, calcium never occurs naturally in the free state although the compounds of the element are widely distributed among geological materials. The main calcium-bearing minerals are: the three carbonates - calcite, ar-

gonite and dolomite; the sulphates - gypsum and anhydrite; and fluorites in the form of fluorite or fluorspar. Calcite is the major constituent of sedimentary rocks such as limestone, chalk, marble, dolomite, eggshells, and pearls, while aragonite is the main components of stalactites and stalagmites. Besides its wide application [2-5], limestone is also the main mineral used for metallic calcium production.

Calcium is an excellent reducing agent, and at elevated temperatures it reacts with oxides or halides of almost all metallic elements to form the corresponding metal. Calcium is used in lead refining (for removal of bismuth), steel refining (as a desulphurizer and deoxidizer) and as an alloying agent for aluminum, silicon and lead. Calcium is also used in the recovery of refractory metals (*e.g.*, chromium, rare earth metals and thorium) from their oxides and in the reduction of uranium dioxide [3].

Correspondence: A. Patarić, Institute for Technology of Nuclear and Other Mineral Raw Materials, Bulevar Franše d'Eperea 86, 11000 Belgrade, Serbia.

E-mail: [a.pataric@itnms.ac.rs](mailto:a.pataric@itnms.ac.rs)

Paper received: 17 August, 2012

Paper revised: 12 June, 2013

Paper accepted: 18 June, 2013

For the first time, in 1808, Davy prepared calcium by electrolysis of anhydrous, molten calcium chloride [4]. Over time, this old electrolysis process for making calcium has been mainly substituted with metallothermic processes. Now, pure calcium metal is made by metallothermic reduction on an industrial scale by reducing calcium oxide with molten silicon or aluminium. Pure limestone or calcite is calcinated in a kiln at 1000 °C to produce calcium oxide for aluminothermic reduction. The thermal decomposition of calcite has been the subject of extensive research over the last 50 years [5-11]. Hills [6] investigated the calcium carbonate decomposition, and showed that the decomposition reaction takes place on a definite boundary between the undecomposed carbonate, and the layer of porous lime formed outside it. The rate of the reaction is controlled by the transfer of heat to this reaction boundary, and by the transfer of CO<sub>2</sub> away from it. Calcium oxide is ground and mixed with aluminum powder. The mixture is heated up to 1200 °C, and the reduction begins producing calcium metal and calcium aluminates [12]. The calcium is removed from the slag by distillation in a vacuum and is being condensed in a cold mold. Calcium alloys are produced industrially by various techniques such as direct alloying or chemical reduction of the raw components.

The purpose of this experimental investigation was to define a technological scheme of the aluminothermic process for calcium metal production from Serbian carbonate mineral raw materials. Also, the basic technological parameters of the particular process phases and necessary equipment for the different technological operations were determined.

## EXPERIMENTAL

There are numerous limestone deposits that can be used as a basis for elemental calcium production

in Serbia. Two samples from the deposits nearby Čačak ("C I" and "C II") and one sample from the deposit "Strezovac" (S) were used in the calcination and reduction experiments, due to the high calcium content. These samples were firstly prepared by grinding.

The dissociation degree dependence on temperature, time and sample size was investigated in order to determine the optimal conditions for calcination process. The dissociation degree of calcium carbonate was determined based on the weight changes of the samples during the calcinations process.

The apparatus scheme for investigation calcination of calcium carbonate is shown in Figure 1. The quartz reaction tube (1) heats up in resistance furnace (7). The thermocouple is used for temperature measuring (5). The speed of nitrogen inlet is regulated by flow meter (6). The outgoing gas is over triple gas outlet pipe (2) being directed to the exit through the rinsing flask (4) or the gas analysis burette (3).

The investigation of dissociation degree at -0.14, +0.14, -5 and +5 15 mm particle size fractions was done at the same apparatus, after grinding and sieving to obtain the appropriate sample size.

The aluminothermic reduction of calcium oxide obtained from dissociation of calcium carbonate was carried out in a laboratory heat-resisting steel retort. The scheme is shown in Figure 2. The aluminum powder is used as the reducing agent. Samples of calcium oxide and aluminum mixtures were pressed on hydraulic press at pressure of 15 MPa, and briquettes with volume density of 2-2.2 kg/dm<sup>3</sup> were obtained.

The retort body (2) is a heat resisting steel tube. The retort bottom is calotte-shaped (1) and the flange (3) with a rubber seal (4) is on the top of the cover, which is water cooled (5). The retort is over a pipe flange (6) connected to vacuum system. The conden-

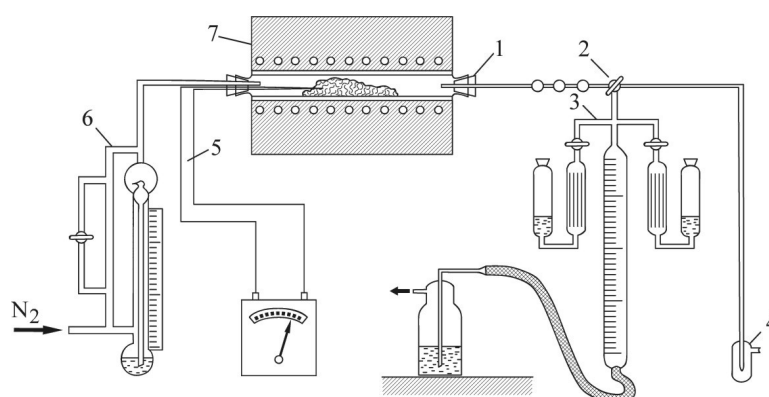


Figure 1. Experimental set-up for the CaCO<sub>3</sub> dissociation process: 1 - reaction tube, 2 - outlet pipe, 3 - gas burette, 4 - rinsing flask, 5 - thermocouple, 6 - flow meter and 7 - resistance furnace.

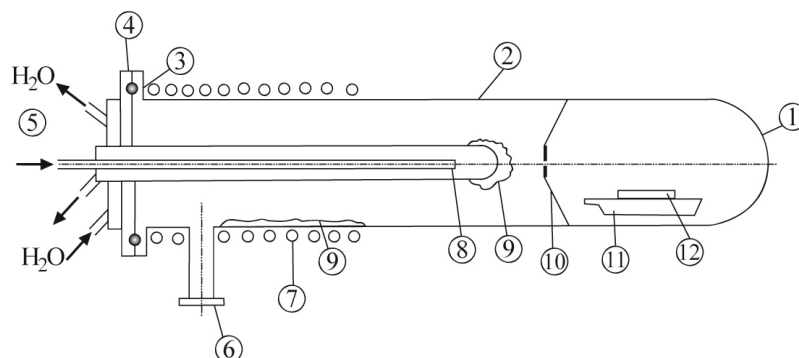


Figure 2. The retort for aluminothermic reduction process of CaO: 1 - retort bottom, 2 - retort body, 3 - flange, 4 - rubber seal, 5 - water cooling, 6 - pipe flange, 7 - copper spiral, 8 - water cooled pipe, 9 - calcium condensate, 10 - funnel screen, 11 - stainless crucible and 12 - bricket.

ser is a water cooled pipe (8), at which is formed calcium condensate (9). Thin layer of calcium condensate is also formed on the retort walls cooled with cooper spiral (7). The funnel-shaped screen (10) with the 25 mm diameter hole is placed in the retort for separation the metal vapor condensation room from the reduction room. The stainless crucible (11) with bricket (12) is placed in the reduction room.

The retort is being heated up to the reduction temperature in the resistance furnace with silicate sticks. The vacuum system is connected through the retort flange (6) and flexible metallic pipe.

The crucible with prepared briquettes for reduction was put into the retort and both were placed in the chamber furnace equipped with the vacuum system.

To allow moisture evaporation, the retort was left open up to 300 °C. Afterwards it was closed, the vacuum system was turned on and the retort heated up to 1200 °C. It was observed that the pressure in the system increased in the temperature range of 600-700 °C, as a result of the degassing process. The heating up to 1200 °C lasted about 5 h, while the reduction process in all experiments lasted 2 h. Thereafter, the retort was taken out from the furnace and cooled under the vacuum. After opening, the metallic calcium was removed from condenser and placed in a desiccator. It was impossible to remove a fine layer of condensate from the retort walls because its highly developed surface was burned upon a touch. The reduction degree was determined based on the amount and composition of the remaining slag, due to the inability to remove all the condensate.

To determine the chemical composition of limestone, slag and metallic calcium, the samples were dissolved in mineral acids. The content of calcium and magnesium was determined by volumetric (complexometric) methods, while the content of other admixtures was determined by atomic absorption

spectroscopy using a Perkin Elmer Analyst 300 spectrometer. To determine the calcination loss, the limestone was calcined at 1100 °C.

The phase and mineralogy composition of limestone samples were determined by XRD (X-ray diffraction) using a Philips PW-1710 diffractometer and transmitted light microscopy (Carl Zeiss-Jena, LENAPOL-U).

Differential thermal analysis/Thermo-gravimetric analysis (DTA/TG) analysis of the samples, each of 100 mg, was carried out on a Derivatograf 1500 device in air atmosphere, using alumina as the reference material, with the heating rate of 10 °C/min.

## RESULTS AND DISCUSSION

The chemical composition of the limestone samples is presented in Table 1. In comparison with the required limestone composition for aluminothermic process (54.5% CaO, up to 2.5% R<sub>2</sub>O<sub>3</sub> (Al<sub>2</sub>O<sub>3</sub>+Fe<sub>2</sub>O<sub>3</sub>), 0.5% MgO and 0.1% Na<sub>2</sub>O+K<sub>2</sub>O), the samples (Table 1) are not high-grade. The contents of CaO and R<sub>2</sub>O<sub>3</sub> are satisfying, while the contents of MgO and Na<sub>2</sub>O+K<sub>2</sub>O are higher than the required amounts.

Table 1. The chemical composition (%) of used limestone samples

Component	Sample		
	C I	C II	S
CaO	53.65	53.72	54.13
MgO	1.18	1.52	0.98
Al <sub>2</sub> O <sub>3</sub>	0.19	0.03	0.13
Fe <sub>2</sub> O <sub>3</sub>	0.15	0.18	0.24
SiO <sub>2</sub>	1.21	0.39	0.67
Na <sub>2</sub> O	0.09	0.16	0.19
K <sub>2</sub> O	0.03	0.02	0.05
Loss of annealing	43.36	43.88	43.48

The X-ray diffraction analysis and light microscopy were used to determine the mineralogy and phase composition of samples. The X-ray diffractograms of the samples with minimum and maximum magnesium content (S and C II) are presented in Figure 3a and b. Figure 3a shows the presence of calcite, while Figure 3b shows the presence of calcite and dolomite.

Crystals and aggregates of calcite are shown in Figure 4, obtained by transmitted light microscopy.

The DTA/TG analysis of the limestone samples is presented in Figure 5. The obtained DTA curves of both C I and C II samples show endothermic peaks, because the dissociation process is followed by endothermic heat effect. Since the DTA curves show only one clearly defined peak, it can be concluded that the calcium carbonate is solely in the form of calcite, while aragonite is not present in the samples.

#### Calcination of calcium carbonate

The calcium carbonate dissociation degree dependence on temperature and time is shown at

Figures 6-8. The dissociation degree dependence on grain size and time for the S sample is shown in Figure 9.

The process rate can be assessed by measuring the dissociation degree dependence on time and temperature. From these measurements it can be concluded that the dissociation rate is approximately the same at appropriate temperatures, for both sample site “Čačak” samples C I and C II (Figures 6 and 7). Thus, the dissociation is completed in 10 min at temperature of 1200 °C, and in 30 min at 1050 °C. The dissociation rate for sample “Strezovac” (S) is slightly lower, so the process is completed in 15 min at 1200 °C, and in 45 min at 1050 °C. The reason for this is significantly higher proportion of calcite larger particles in the sample S.

The investigation of the limestone particle size influence on the process rate shows as expected that the process rate increases by grinding the limestone (Figure 9). When fragmentation is less than 5 mm, the process rate does not differ significantly, because the

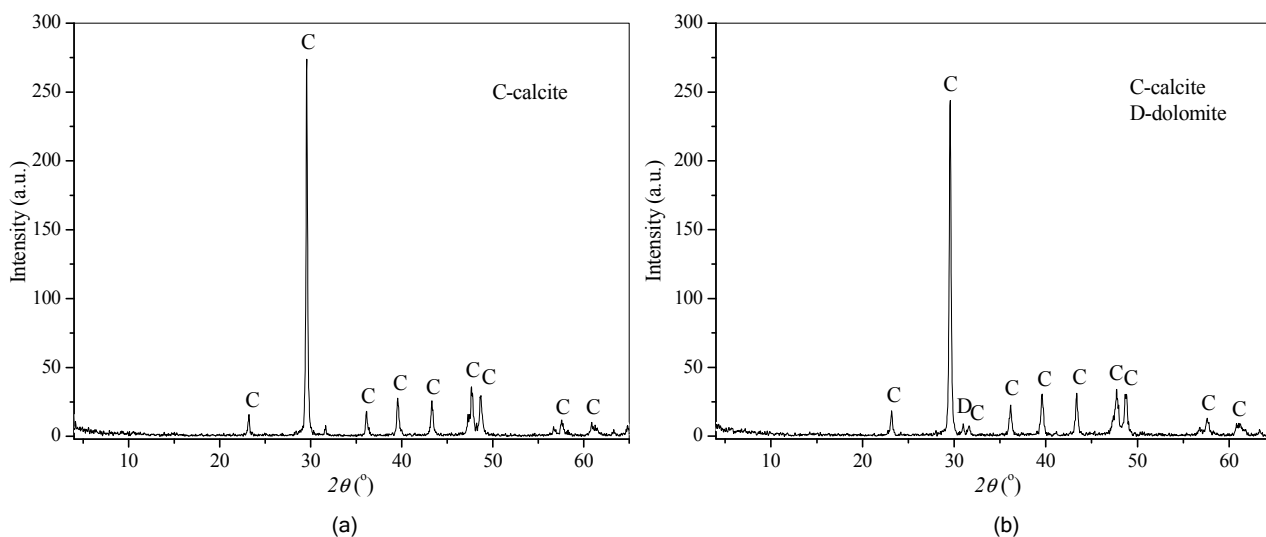


Figure 3. X-Ray diffractogram of the S (a) and C II sample (b).

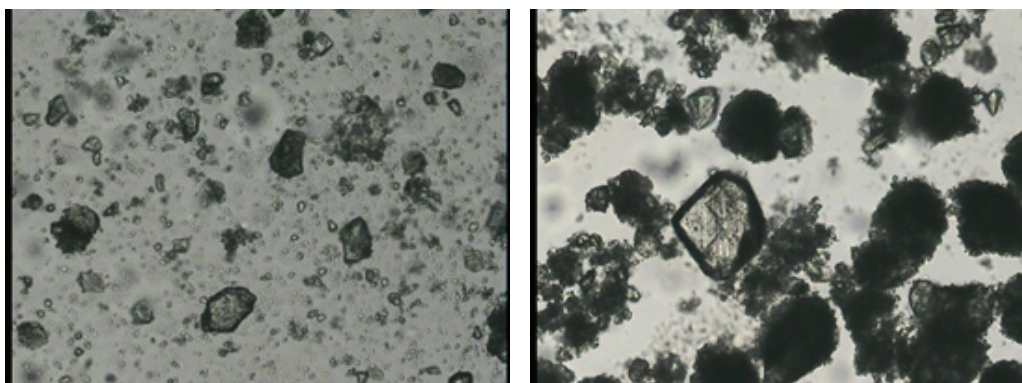


Figure 4. Crystals and aggregates of calcite: Magnification: 10x, II nicols.

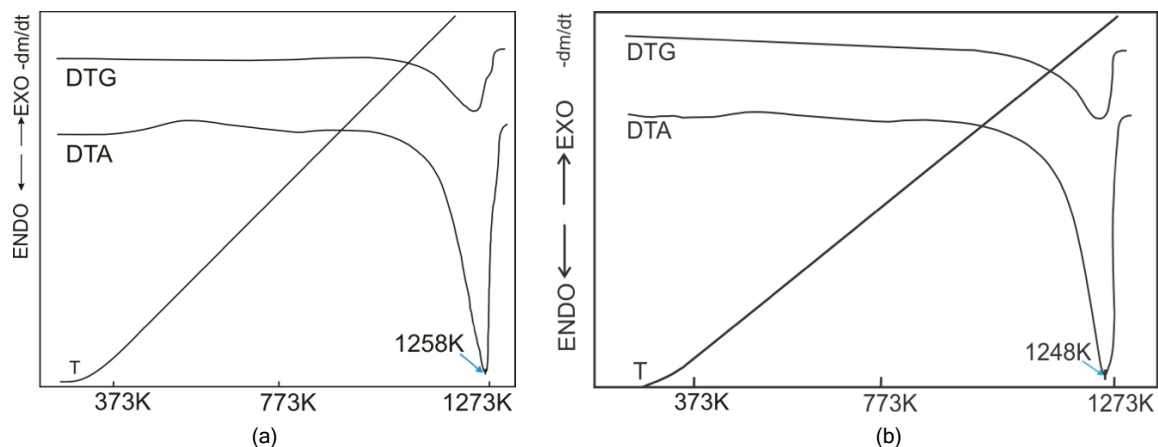


Figure 5. DTA/TG Analysis of the C I (a) and C II sample (b).

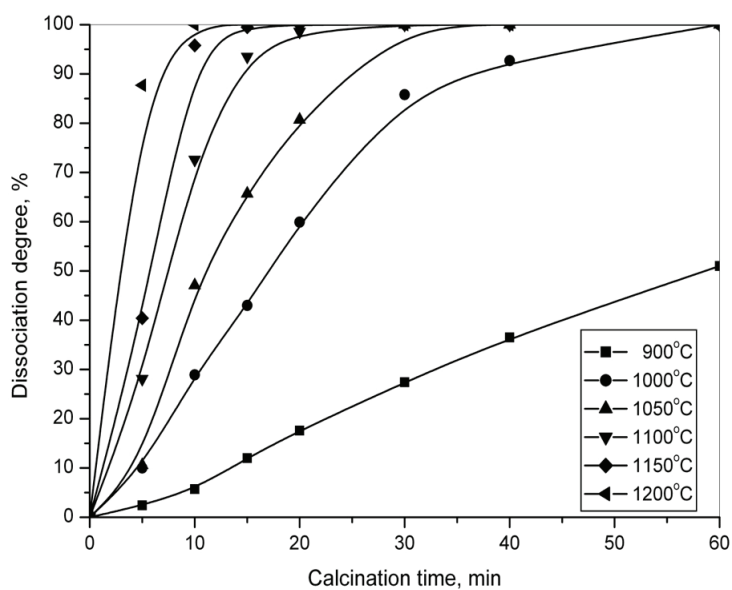


Figure 6. The dissociation degree dependence on the temperature and time for the C I sample.

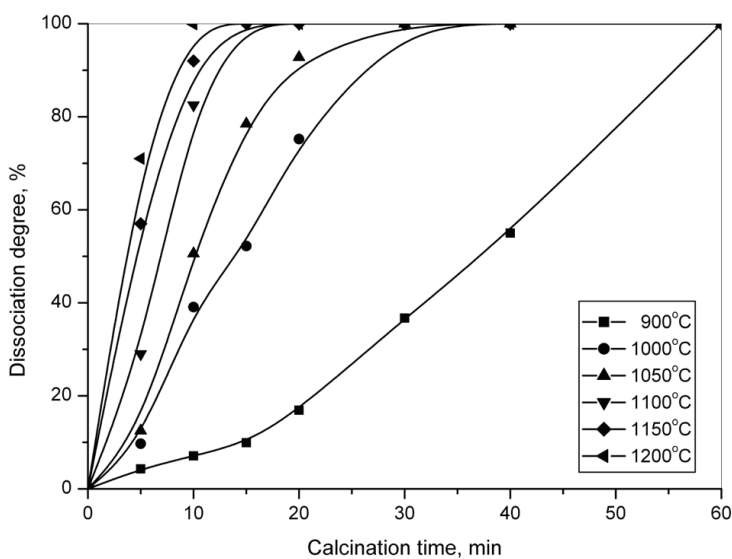


Figure 7. The dissociation degree dependence on the temperature and time for the C II sample.

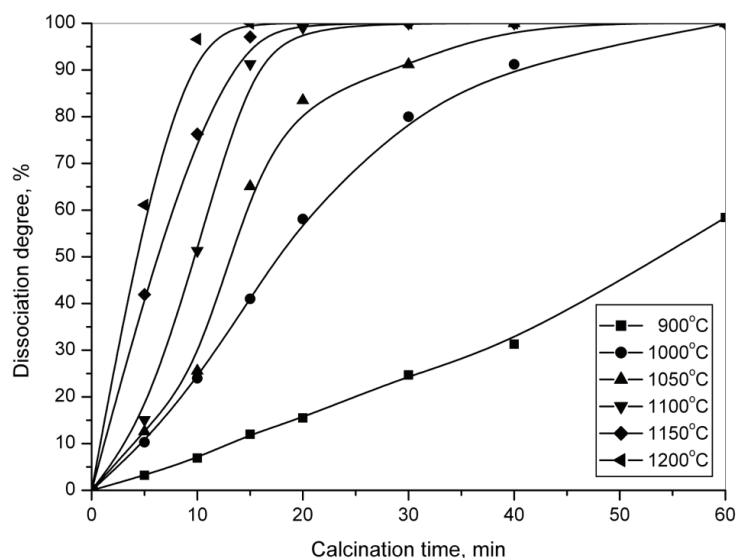


Figure 8. The dissociation degree dependence on the temperature and time for the S sample.

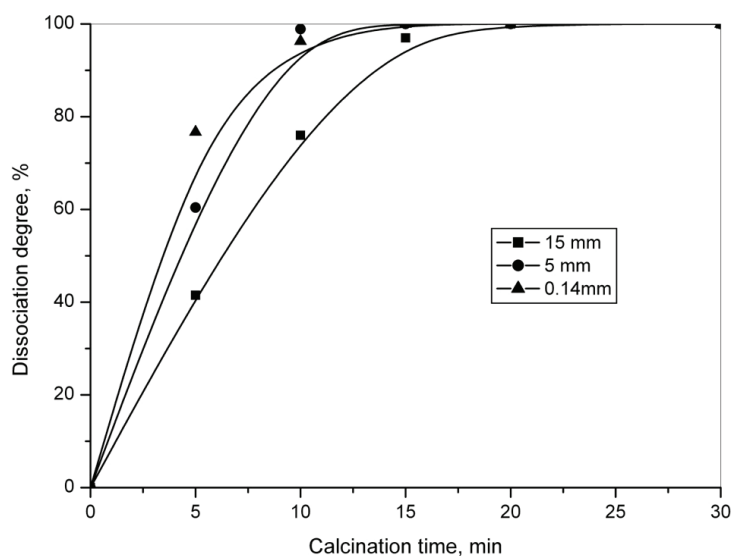


Figure 9. The dissociation degree dependence on the granulation at 1150 °C for the S sample.

maximum dissociation degree is achieved in approximately the same time of 15 min. The required quantity of calcium oxide needed for aluminothermic reduction was determined after the dissociation process.

#### Calcium oxide aluminothermy

For reduction process with aluminum the three samples of calcium oxide were used:

- the sample of calcium oxide obtained from limestone calcination deposit "C I",
- the sample of calcium oxide obtained from limestone calcination deposit "C II" and
- the sample of calcium oxide obtained from limestone calcination deposit "S".

The chemical composition of calcium oxide samples is presented in Table 2.

Table 2. The chemical composition of calcium oxide (%)

Component	Sample		
	C I	C II	S
CaO	94.71	95.68	95.79
MgO	2.09	2.73	1.74
Al <sub>2</sub> O <sub>3</sub>	0.38	0.06	0.25
Fe <sub>2</sub> O <sub>3</sub>	0.24	0.34	0.43
SiO <sub>2</sub>	2.17	0.69	1.16
Na <sub>2</sub> O	0.18	0.29	0.34
K <sub>2</sub> O	0.054	0.04	0.08

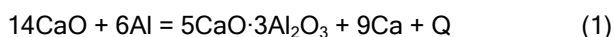
The chemical composition of calcium oxide shows increased content of magnesium oxide and alkaline oxides (especially sodium), Table 2, which is undesirable for the calcium aluminothermic process.

Magnesium oxide and alkaline oxides (sodium and potassium) are reduced together with calcium. Being easily evaporative metals, they evaporate at lower temperatures than the calcium and they are being condensed together with calcium. Metal obtained in this way has increased content of magnesium and alkaline metals. The manipulation with metallic calcium, which has increased content of alkaline metals, is very difficult because of their high reactivity and ignitability. Weight loss of calcium oxide due to calcination should not exceed 0.2%. For this reason, the calcium oxide obtained by calcination process must be protected from moisture and carbon dioxide absorption before aluminothermy process.

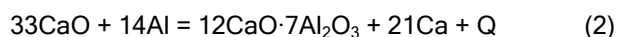
The discontinuous retort process was chosen for laboratory investigation of calcium oxide reduction. Charge preparation for reduction was carried out by mixing of components and their briquetting. The aluminum powder is used as the reducing agent. The measured amount of calcium oxide and aluminum powder samples were homogenized by long-term mixing.

The briquettes had satisfactory strength and did not smash by falling to the floor from a height of 0.7 m. The values of 6.8 MPa was obtained by crushing resistance testing at the hydraulic press. However, it should be noted that the briquettes should be charged in the reduction retort immediately after pressing, because they could be broken up after a few hours due to absorption of moisture and carbon dioxide from the air; otherwise they must be stored in hermetic containers.

Aluminothermic reduction process is carried out according to the following reaction:



which can be replaced by:



Stoichiometric amount of aluminum, calculated according to Eq. (2) is 17 wt.% of charge. The charge with 20 wt.% Al was used for experiments. The required vacuum for conducting experiments was at least 3 kPa, to prevent oxidation of obtained calcium [13]. The satisfying rate of reduction process is carried out at temperature of at least 1200 °C. Due to the highly exothermic process, the charge for experiments weighed only 0.1 kg, so the reduction was completed within 2 h.

Calcium metal vapors originated in the reaction space are directed towards condenser where calcium was condensed. The residual slag after reduction represented a useful refractory material.

The chemical composition of obtained calcium from different starting materials is shown in Table 3.

By analyzing the chemical composition of the obtained calcium (Table 3) it can be concluded that the content of hardly evaporated metals (Fe, Cu, Ni and Si) is very low, what meets the requirements for the calcium of commercial quality. Extremely low content of aluminum indicates that there was no mechanical transfer of aluminum particles to the place where the metallic calcium vapor condensed. It was expected that magnesium, sodium and potassium contents are higher in calcium, because the contents of these metals were higher than allowed in the starting material. Since these metals are reduced by aluminum and since they are more evaporative than calcium, they condensed together. As the condenser construction did not allow fractional condensation of metal vapors, their presence in calcium was inevitable.

Table 3. Impurities content in calcium (%)

Component	Sample			
	CI	CII	S	Ca, commercial grade
Fe	0.006	0.0074	0.010	0.01
Cu	0.040	0.025	0.033	0.05
Ni	0.003	0.007	0.005	0.01
Mn	0.150	0.190	0.170	0.10
Al	0.015	0.023	0.006	0.50
Si	0.065	0.001	0.016	0.20
Mg	3.360	4.170	2.750	0.10
Na	0.290	0.450	0.590	-
K	0.082	0.064	0.119	-

The vacuum refining distillation with fractional condensation of metal vapors in a specially constructed condenser was necessary to obtain calcium refined from impurities. Residual slag after reduction process in the form of solid sintered product remains in the crucible. After grinding, the chemical composition of slag samples was examined and it is presented in Table 4. The ratio of CaO and Al<sub>2</sub>O<sub>3</sub> in the slag according to the phase diagram of CaO-Al<sub>2</sub>O<sub>3</sub> system [14] shows that the metallothermic reduction process does not occur, according to Eq. (2).

Table 4. The chemical composition of slags (%)

Component	Sample		
	CI	CII	S
CaO	54.70	57.38	55.62
Al+Al <sub>2</sub> O <sub>3</sub>	39.68	38.96	40.08
MgO	0.98	1.44	0.88
Fe <sub>2</sub> O <sub>3</sub>	0.51	0.63	0.81
SiO <sub>2</sub>	3.85	1.31	2.15
Na <sub>2</sub> O	0.09	0.12	0.17
K <sub>2</sub> O	0.034	0.031	0.0425

## CONCLUSION

Increased content of magnesium, sodium and potassium was determined by chemical analysis of limestone. XRD and light microscopy analysis showed that calcium is present in the form of calcite and dolomite, and the magnesium in the form of dolomite.

The examination of calcium carbonate dissociation shows that the dissociation rate is approximately the same at appropriate temperatures. Thus, the dissociation is completed in 10 min at 1200 °C, and in 30 min at 1050 °C. The dissociation rate for sample "Strezovac" is slightly lower, so the process is completed in 15 min at 1200 °C, and in 45 min at 1050 °C.

The charge was prepared by mixing of components and briquetting. The aluminum powder was used as the reducing agent. The total briquetting pressure was 15 MPa, where the obtained briquettes had a density of 2-2.2 kg/dm<sup>3</sup>.

The charge with 20 wt.% Al was used for experiments. The required vacuum for conducting experiments was at least 3 kPa. The satisfactory rate of reduction process is carried out at temperature of at least 1200 °C. Due to the highly exothermic process, the charge for experiments weighed just 0.1 kg, so the reduction completed within 2 h.

The chemical composition analysis of obtained calcium shows that the content of hardly evaporated metals (Fe, Cu, Ni and Si) is very low. The magnesium, sodium and potassium contents are higher because these metals are reduced by aluminum and they are more evaporative than calcium.

The chemical composition analysis of slag and phase diagram of CaO-Al<sub>2</sub>O<sub>3</sub> system showed that the metallothermic reduction process does not occur, according to Eq. (2).

## ACKNOWLEDGEMENT

The authors wish to acknowledge the financial support from the Ministry of Education, Science and Technological Development of the Republic of Serbia through the projects TR34002 and TR34023.

## REFERENCES

- [1] F. Cardarelli, *Materials handbook: a concise desktop reference*, 2<sup>nd</sup> ed., Springer-Verlag, London, 2008, pp. 620-622
- [2] C.L. Mantell, *The alkaline earth metals: calcium, barium, and strontium*, in: C.A. Hampel (ed.) *Rare Metals Handbook*, 2<sup>nd</sup> ed., Reinhold, New York, 1973, pp. 15-25
- [3] K. Othmer, *Encyclopedia of Chemical Technology*, 4<sup>th</sup> ed., Wiley-VCH, New York, 1992, pp. 777-782
- [4] C.L. Mantell, C. Hardy, *Calcium Metallurgy and Technology*, Reinhold, New York, 1945, p. 358
- [5] X. Jia, G. Cheng-Fu, J. Yong-Gang, W. Yong-He, J. Cent. South Univ. Technol. **17** (2010) 918–923
- [6] A.W.D. Hills, *Chem. Eng. Sci.* **23** (1968) 297-320
- [7] P.K. Gallagher, D.W. Jr. Johnson, *Thermochim. Acta* **6** (1973) 67-83
- [8] A.M. Mulokozi, E. Lugwisha, *Thermochim. Acta* **194** (1992) 375-383
- [9] B.V. L'Vov, L.K. Polzik, V.L. Ugolkov, *Thermochim. Acta* **390** (2002) 5-19
- [10] Y.L. Ren, M. Wang, R.S. Li, *J. Therm. Anal. Calorim.* **91** (2008) 867-871
- [11] C. Rodriguez-Navarro, E. Ruiz-Agudo, A.Luque, A.B. Rodriguez-Navarro, M. Ortega-Huertas, *Am. Mineralogists* **94** (2009) 578-593
- [12] D. Beruto, A.W. Searcy, M.G. Kim, *Thermochim. Acta* **424** (2004) 99-109
- [13] K.T. Jacob, S. Srikanth, *High Temp. Mater. Processes* **9** (1990) 77-92
- [14] R.W. Nurse, J.H. Welch, *Trans. Brit. Ceram. Soc.* **64** (1965) 409-418.



MIROSLAV SOKIĆ  
VLADISLAV MATKOVIĆ  
BRANISLAV MARKOVIĆ  
ZVONKO GULIŠIJA  
ALEKSANDRA PATARIĆ  
MARIJA MIHAILOVIĆ  
ZORAN JANJUŠEVIĆ

Institut za tehnologiju, nuklearnih i  
drugih mineralnih sirovina, Beograd,  
Srbija

NAUČNI RAD

## MOGUĆNOSTI DOBIJANJA KALCIJUMA IZ KARBONATNIH MINERALNIH SIROVINA REPUBLIKE SRBIJE

*Eksperimentalnim istraživanjima su definisani kako tehnološka šema dobijanja kalcijuma iz krečnjaka aluminotermijskim procesom tako i osnovni radni parametri pojedinih tehnoloških faza. Uzorci krečnjaka koji su korišćeni u radu imaju visok sadržaj Mg, Na i K. Rendgenska analiza je pokazala da uzorci uglavnom sadrže kalcit i u manjoj količini dolomit. Na početku je ispitan uticaj temperature, vremena i granulometrijskog sastava na kalcinaciju kalcijum-karbonata. Vreme trajanja procesa disocijacije je 10-15 min na 1200 °C i povećava se sa smanjenjem veličine čestica do 5 mm. Nakon toga, ispitana je aluminotermijska redukcija kalcijum-oksida. Na temperaturi od 1200 °C i vakuumu od 3 KPa proces redukcije se završava za 2 h. Analiza hemijskog sastava kalcijum-oksida i kalcijuma pokazuje povećan sadržaj magnezijum-oksida i oksida alkalnih metala, posebno natrijuma.*

*Ključne reči: krečnjak, kalcinacija, kalcijum-oksid, aluminotermija, kalcijum.*