

## **Application of industrial wastes in renewable energy production**

K. Rugele<sup>1,2,\*</sup>, G. Bumanis<sup>3</sup>, L. Mezule<sup>1</sup>, T. Juhna<sup>1</sup> and D. Bajare<sup>3</sup>

<sup>1</sup>Riga Technical University, Faculty of Civil Engineering, Department of Water Engineering and Technology, Kalku 1, LV1047 Riga, Latvia

<sup>2</sup>Riga Technical University, Faculty of Materials Science and Applied Chemistry, Institute of General Chemical Engineering, Kalku 1, LV1047 Riga, Latvia,

<sup>3</sup>Riga Technical University, Faculty of Civil Engineering, Department of Building Materials and Products, Kalku 1, LV1047 Riga, Latvia

\*Correspondence: kristine.rugele@rtu.lv

**Abstract.** This research focuses on the industrial waste application as raw materials to create composite material and its characterisation for their possible application in anaerobic digestion. As the limitation of effective biogas digestion process is associated with inhibition of the some elements and acidification of biodegradable organic matter, therefore a highly porous alkaline composite material was evaluated in this research as buffer capacity increasing material. Batch experiments were provided with composite material additive in anaerobic digesters. Results indicate that alkaline composite materials in anaerobic digesters treated acidic whey could increase BMP up to 22%, but pH value could be kept in the optimal range (7.2–7.4) to ensure the effective digestion process.

**Key words:** biogas, anaerobic digestion, alkaline composite material.

### **INTRODUCTION**

The use of industrial waste to produce energy and reduce environmental pollution is a very attractive topic. Whey is the most important waste and pollutant in dairy industry. Despite the high potential for waste reduction and energy production, anaerobic digestion is not widespread in the dairy industry (Chatzipaschali et al., 2012). This is largely due to the problem of slow reaction rates which require long hydraulic retention time (HRT) and poor process stability (Rugele et al., 2013). However, the treatment of whey by anaerobic digestion is a solution to minimise the environmental impact and, at the same time, convert waste into energy, which could be further consumed in production process (Siso, 1996).

The amount of industrial waste is growing, which makes recycling possibility a very significant challenge nowadays. More than 3,760 t of glass fibre waste and 100 t of metal manufacturing waste were disposed in landfills in Latvia in 2012. However, diverting non-hazardous industrial and manufacturing by-products to recycling saves disposal costs and preserves natural resources by decreasing the demand for virgin materials. Alkali activated composite matrices (CM) or geopolymers could be created from wide group of alumina and silica contained waste. Geopolymers are similar to zeolites in chemical composition, but they reveal an amorphous microstructure, which

are forming by the co-polymerisation of individual alumino and silicate species, which originate from the dissolution of silicon and aluminium containing source materials at a high pH in the presence of soluble alkali metal silicates. It has been shown before that geopolymerisation can transform a wide range of waste alumino-silicate materials into building and mining materials with excellent chemical and physical properties (Xu et al., 2000). During the production of CM, reutilization of industrial waste materials takes place, thus, making the technology environmentally friendly.

The use of industrial waste and food industry residues to produce energy is a new challenge in our recycling society and creates a novel point of view in ‘waste to energy’ topic. The potential use of alkali-releasing composite materials from industrial wastes for pH control within the anaerobic treatment process of whey was evaluated in this study. The alkali-releasing material was produced from aluminium and glass fibre production waste since it has the potential for long term pH stabilization and can act as a support for microorganism immobilisation (Rugele et al., 2014).

## MATERIALS AND METHODS

### Composite matrices (CM)

CM consisted of alumina and silica rich materials and was activated by modified sodium silicate solution. Porous composite matrices used for stabilization of pH during anaerobic digestion process was created from aluminium scrap recycling waste (ASRW), silicate glass (SG) and metakaolin (MK). MK and aluminium scrap recycling waste was used as alumina source in CM. MK, SG and sodium silicate solution was the silica source. The alkali source was sodium silicate solution and SG. The chemical composition of raw materials is given in Table 1 and it was determined according to LVS EN-196-2 with sensibility  $\pm 0.5$  w%.

**Table 1.** Chemical composition of raw materials

Chemical component	ASRW (w%)	MK (w%)	SG (w%)
Al <sub>2</sub> O <sub>3</sub>	63.19	51.7	1.03
SiO <sub>2</sub>	7.92	34.4	68.07
CaO	2.57	0.09	1.39
SO <sub>3</sub>	0.36	–	–
TiO <sub>2</sub>	0.53	0.55	–
MgO	4.43	0.13	–
Fe <sub>2</sub> O <sub>3</sub>	4.54	0.53	0.19

The metakaolin (MK) was generated in the Material research laboratory of Institute of Materials and Structures (RTU) by calcination of commercial kaolin clay containing minor quartz impurities. Calcination of kaolin clay was carried out at 800 °C in an air atmosphere rotary furnace for approximately 30 min in maximum temperature. MK was ground in the laboratory planetary ball mill Retsch PM 400 for 30 min with speed 300 rpm. Specific surface area of ground MK was 15.86 m<sup>2</sup> g<sup>-1</sup> (detected by BET method, Nova 1200 E-Series, Quantachrome Instruments), but effective diameter of MK particles was 743.1 nm (detected by Zeta potential, 90 Plus and MAS ZetaPALS Brookhaven Instruments). The crystalline layer structure, which is a common characteristic of clay

minerals, had a fine particle size (1–3  $\mu\text{m}$ ) and plate like morphology (detected by SEM, TESCAN Mira\LMU Field-Emission-Gun). According to XRD analyses (Rigaku Ultima+) the produced MK was largely amorphous, with a small quantity of quartz ( $\text{SiO}_2$ ) as an impurity phase and low amount of kaolin.

The sodium silicate solution was created from sodium silicate solution ( $\text{Na}_2\text{SiO}_3 + n\text{H}_2\text{O}$ ) and sodium hydroxide ( $\text{NaOH}$ , purity 97%) to increase alkalinity of solution.

Mixture design of CM was calculated with the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  mass ratio 1.8 and  $\text{SiO}_2/\text{Na}_2\text{O} - 3.67$ ,  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 - 0.5$  respectively. The porous structure of CM develops from gasses which are released from aluminium scrap recycling wastes mixed with sodium silicate solution. Material was moulded in 40 x 40 x 160 mm moulds. After expansion of the green material it was cured at temperature 80  $^\circ\text{C}$  for 24 h.

After demoulding physical properties, such as density, water absorption, open and total porosity were determined for CM in accordance with EN 1097-6 and EN 1097-7. Mechanical properties were determined according to LVS EN 1015-11.

Alkalinity is defined as a measure of the buffering capacity of water to neutralize acid. High alkalinity in water indicates increased buffering capacity. Buffer capacity was tested for 3 days old CM by immersing cubical specimens (weight  $3.5 \pm 0.5$  g) in deionized water and measuring the alkalinity dynamics within 30 days. Samples were moved to a new bath with deionized water (100 ml) each 24 h. pH of water solution was determined and alkalinity was calculated with strong acid-strong base titration method. The pH at the equivalence point for this titration was 7.0.

For anaerobic digestion in batch experimental setup CM granules with size 2/4 mm and 4/8 mm were prepared.

### Cheese whey and inoculum

The cheese whey was supplied by a dairy product manufacturer ‘Vecsiljani Ltd’ (Latvia). The inoculum was supplied by a municipal waste water treatment plant. Prior experiments the inoculum was kept at 37  $^\circ\text{C}$  for 2 days to stabilize the microorganisms. The characteristic values of chemical analysis of the cheese whey and inoculum used are presented in Table 2. Whey sample had a high level of TS (total solids – 6.48%) and VS (volatile solids – 5.89%). Whey at the same time showed to be a high strength organic substrate – COD (chemical oxygen demand) value was as high as 58.8 g  $\text{O}_2$   $\text{L}^{-1}$ , whereas the main organic component was lactose contributing to 4.2% of the total mass.

**Table 2.** Chemical composition of raw materials

Parameter	Inoculum	Whey
pH (20 $^\circ\text{C}$ )	–	6.48
total solids (% w w $^{-1}$ )	5.78	5.89
volatile solids (% w w $^{-1}$ )	4.35	5.25
COD <sub>total</sub> (g $\text{O}_2$ $\text{L}^{-1}$ )	–	58.8
ash (% w w $^{-1}$ )	0.87	0.69
protein (% w w $^{-1}$ )	–	0.5
lactose (% w w $^{-1}$ )	–	4.2
fat (% w w $^{-1}$ )	–	0.05

### **Experimental setup**

Batch experiments were carried out in glass reactors with working volume of 100 mL. Prepared CM granules were added at the beginning of the experiment without any previous pH correction. Whey concentration was 15%. The reactors were incubated at  $37 \pm 0.5$  °C. The mass ratio between CM granules and VS of substrate were constant 0.6 ( $\text{g}_{\text{AAM}} \text{g}^{-1} \text{VS}$ ).

Dilution process or any other pre-treatment of whey was not used. During the experiments the biogas production and gas content was controlled after each 12 hours.

The TS and VS solids were measured both for the whey and inoculum at the beginning and at the end of the fermentation for each reactor. pH was measured every 48 hours.

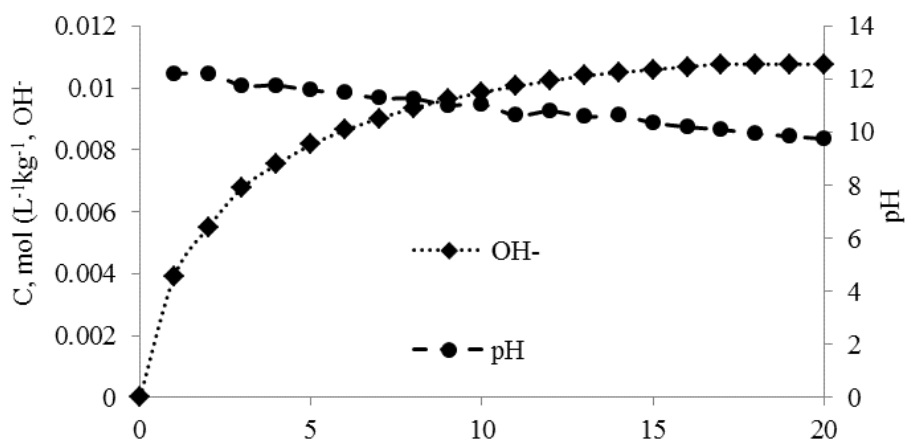
For the analysis of anaerobic digestion tests volatile organic fatty acids (VOA) content were measured by titration (FOS/TAC measurements according to Nordmann method) method with 0.1 M  $\text{H}_2\text{SO}_4$ . TS were determined by drying a sample at 105 °C for 24 hours. VS and ash were analyzed at 550 °C in muffle furnace for 150 minutes. COD was analyzed with Hach Lange cuvettes test. The pH was measured using pH-meter Lutron pH-208. Produced methane was measured with syringes contained 3M NaOH. Each sample average of three measurements was performed.

## **RESULTS AND DISCUSSION**

### **CM characterisation**

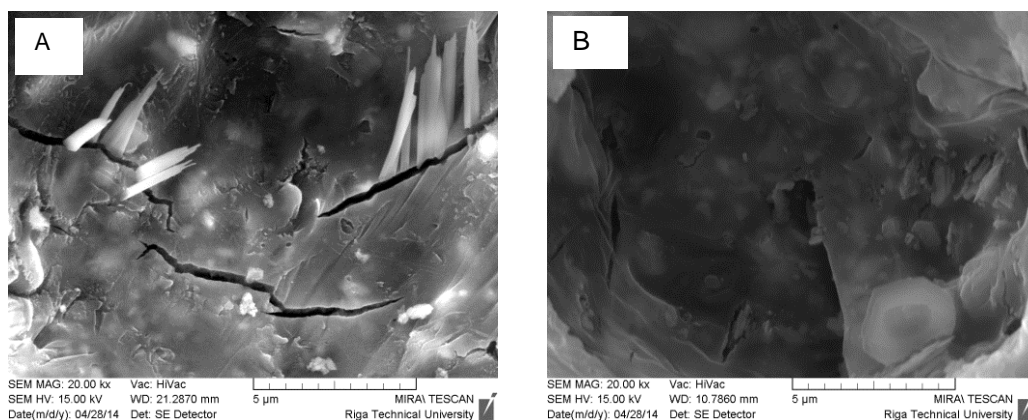
The most leachable species in CM during titration test are the  $\text{Na}^+$  and  $\text{OH}^-$  ions from (alkaline) pore water transfer to leachates, and framework dissolution by alkali/ $\text{H}_3\text{O}^+$  ion exchange (Aly et al., 2008). Under optimal conditions the rate of alkali release would reflect the mobility of the alkalis in the paste. The migration of ions affects pore volume and pore solution composition, both of which affect the amount of alkali being released from the MC.

The initial pH level of water solution with CM granules was 12.5. During the first day immersion 35 to 40% of total  $\text{OH}^-$  amount leached therefore high initial buffer capacity can be ensured. This can be explained by the rapid solution of free alkali layer based on pore walls. After dissolution of basic layer, further  $\text{OH}^-$  leaching decreased and after 16 days it reached a maximum of  $0.0108 \text{ mol L}^{-1} \text{ kg}^{-1} \text{ CM}$  (Fig. 1). Slow alkali leaching after first days can be contributed to the solution of alkalis trapped in micropores and inside the structure of material. The leaching from deeper layers of material was retarded due to closed material structure in the deeper layers. The pH level decreased continuously and at the day 20 it dropped down to pH 10.2. Although the pH level of water solution was still high, the buffer capacity of leachate was low. Thus, to ensure prolonged and effective pH control, the proper dosage of CM must be provided. This value could be defined by the pH decrease in the biogas reactors and, to ensure optional pH level in reactor, proper calculations must be provided.



**Figure 1.** OH<sup>-</sup> leaching in water and pH after CM removal.

To confirm that the leachate comes from alkaline crystals on pore surface microstructure analyses of granules were performed (Fig. 2). The granule pore surface was free of alkali layer and confirmed the assumption. SEM micrographs indicated that the CM structure was with more micropores and less solid when compared to granule structure before leaching test and no crystals on CM granule surface was present (Fig. 2B). SEM micrograph after leaching test confirmed the increase of BET surface area by revealing highly porous microstructure of CM after leaching test.

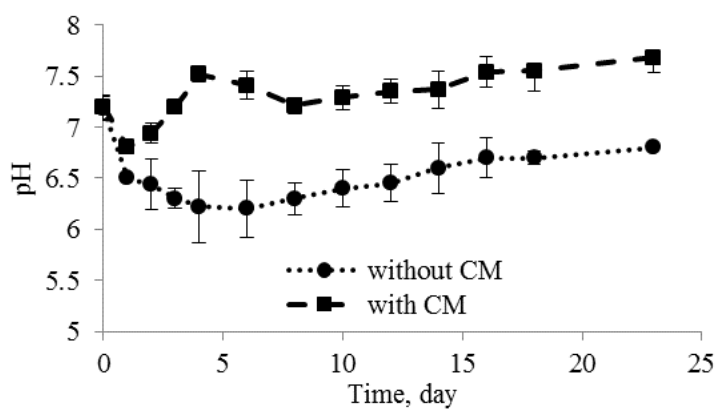


**Figure 2.** Microphotography of porous CM before (A) and after leaching test (B).

### pH level in anaerobic digesters with CM addition

The pH level of batch experiments was analyzed during digestion. Results are showed in Fig. 3. The initial batch pH level at the beginning of test was  $\text{pH } 7.20 \pm 0.12$ . The initial pH level was mainly determined by the amount of whey added to the inoculum. The effect of CM granules on batch pH level was determined. The study showed, that the addition of  $0.6\text{g CM g}^{-1}\text{ VS}$  decreased the pH level to  $6.82 \pm 0.04$  after 24 hours. The digester without CM had a  $\text{pH of } 6.50 \pm 0.05$ . After 3 days pH increased

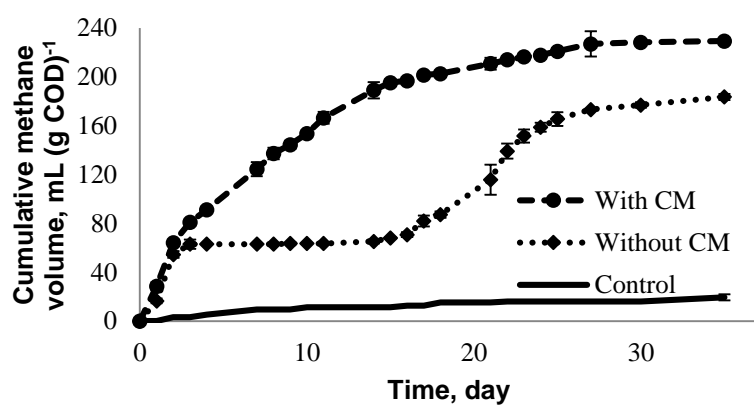
in the digesters with CM, reaching value 7.58 on the 5<sup>th</sup> day, later stable pH around 7.20 was observed. At the end of test pH increased till  $7.68 \pm 0.15$ . pH not increase higher than 6.80 for the digesters without CM.



**Figure 3.** pH values in anaerobic digesters with 15% acid whey and CM addition.

### Biochemical methane potential test

According to the methane production cumulative curves it shows that the addition of the CM improves biogas production (Fig. 4). The curve indicates that anaerobic digestion process was not inhibited by the addition of CM and high concentration of whey. In anaerobic digestion without CM added system inhibition was observed for the first ten days and BMP value was 22% lower.



**Figure 4.** Cumulative methane curves with and without CM addition.

At the end of the experiment much higher VOA amount was observed in the reactors without CM addition, what indicated on process inhibition. Soluble COD showed better substrate degradation rate in reactors with material additive.

**Table 3.** Results in the end of batch experiment with CM and acidic whey

Sample	BMP, ml <sub>CH4</sub> g <sup>-1</sup>	pH	VOA, g kg <sup>-1</sup>	VS, g kg <sup>-1</sup>	COD reduction, %
with CM	328±12	7.68±0.05	1.81±0.07	4.11 ± 1.13	89.8±2.1
without CM	256±32	6.80±0.12	4.37±0.19	4.65 ± 0.44	54.5±3.9
control	15±3	8.20±0.23	0.02±0.003	0.43 ± 0.03	-

Much higher COD reduction (about 35% more) was observed in reactors with added CM, what characterizes a more stable and favourable conditions for the anaerobic microorganisms.

## CONCLUSIONS

Effective waste management could be achieved by using alkali activation technology to create alkali activated porous composite matrices, which could be used in anaerobic digestion process to provide conversion of cheese whey into biogas. Highly porous material with alkaline crystals on the pore surface could be obtained and it can be regarded as potential passive pH controlling system in biotechnologies. It was shown that material from recycled wastes could be used as a new progressive material for enhancement of the anaerobic process. The passive pH controlling system increased pH value and ensured active digestion process up to day 15.

ACKNOWLEDGEMENTS. This work has been supported by ESF project 'Involvement of Human Resources for Development of Integrated Renewable Energy Resources Energy Production System', No. 2013/0014/1DP/1.1.1.2.0/13/APIA/VIAA/026.

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