

An Assessment of Recyclability of Used Aluminium Coffee Capsules

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Abstract

As a result of increasing demands for aluminium in numerous sectors such as construction, automotive and transportation, its rate of consumption has sharply risen in recent decades. Aluminium is also used in containers for food- and drinks packaging due to its good formability, low density and corrosion resistance. The use of aluminium in everyday products lead to complex end-of-life waste, such as coffee capsules, requiring advanced recycling processes to achieve high metal recovery and quality, which is essential to reduce environmental impact and economic cost. This study focuses on the recyclability of used coffee capsules via remelting under a salt flux. Results were evaluated for different aspects such as metal yield, metal purity as well as gas generation during treatment.

Keywords

Recycling • Coffee capsules • Aluminium

Introduction

Primary production of aluminium has been increasing over the last decades as a result of the increase in aluminium consumption in different sectors such as transportation, engineering, and packaging [1]. Recycling is getting more important to reduce cost and improve resource efficiency, i.e.

reduce the energy consumption and environmental impact related to aluminium production [2].

Aluminium in consumer packaging is more challenging to recycle compared with scrap from transportation and buildings due to its low mass and often complex multi-component structure (plastics, paper, pigments etc.) [3]. Used coffee capsules is an example of a packaging which is collected at producer retail outlets. Recycling of collected capsules can, however, be challenging due to their high organic content (coffee residue) and an assessment of suitable recycling methodologies is hence required.

Rather than being collected, these capsules often end up in household waste, which is typically incinerated or landfilled. The bottom ash resulting from incineration will contain aluminium fractions which are still recyclable, however, a certain amount of the metal will be lost due to oxidation during incineration [4]. Hence, customised recycling of collected aluminium scrap is the best option to recover as much as possible of the metal value.

Post-consumer scrap is usually recycled using a chloride-based salt flux to prevent liquid aluminium from oxidation and remove oxides. Addition of fluoride compounds is necessary to enhance the coalescence of aluminium droplets [5]. The current work focuses on the metal recovery from used coffee capsules (with or without a pre-melting heat treatment, with or without residual coffee in the capsules) via remelting under a salt flux. The purity of the recovered aluminium was also established. The study also includes an organic degradation analysis of the off-gas with an online Fourier-transform infrared spectroscopy (FTIR) analyser during heating, targeting detection of the most common hydrocarbons, gases like H₂, CO, CO₂, some halogenated compounds and others.

Experimental Materials and Procedure

In order to simulate customer behaviour, used capsules including residual wet coffee, as well as un-used capsules with and without dry coffee as reference, have been selected

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for this study. Their effect on metal recovery during standard metallurgical recycling operations is evaluated.

Materials and Experimental Matrix

New and used coffee capsules, where coffee remained or had been removed, were used for the recycling and pyrolysis trials. Prior to melting, capsules were mounted in epoxy to characterize the wall thickness, the composition and the capsule coating in the Scanning Electron Microscope with Electron Dispersive Spectroscopy (SEM/EDS). Change in colour and mass were observed during the heating pre-treatment and elemental composition of the resulting metal was analysed via Inductively Coupled Plasma Mass Spectrometry (ICP-MS) after re-melting. Finally, the off-gas composition during capsule pyrolysis and re-melting was monitored using FTIR Spectroscopy

Experimental Procedure

Direct Pyrolysis of Spent Capsules

The pyrolysis experiments were aimed at characterising the off-gases from the capsules when heated and melted. The tests were conducted in a programmable resistance furnace. The unit can reach up to 1600 °C with a maximum heating rate of 600 °C/h. For this particular work a set temperature of 800 °C was selected, with a heating ramp rate of 300 °C/h. The reactor has a volume of 1 L. It contained a pressure gauge, a gas sampling vent, a thermocouple, a carrier gas inlet (Ar) and an exhaust. The reactor was held at the targeted temperature for one hour, after which the furnace was stopped and cooled down naturally. Before starting the experiments, a crucible with a single spent coffee capsule with the coffee residue was placed inside the reactor. The thermocouple (type K NiCr–Ni) was adjusted to the centre of the reactor to detect the furnace temperature above the crucible during the process. The thermocouple was connected to a thermo-logger to record the temperature every 20 s. The reactor was sealed and placed inside the furnace. The exhaust was connected to two sequentially connected bottles (as scrubbers), the first bottle was empty and acted as a safety so that to prevent the liquid in the second bottle entering into the reactor in case of pressure loss in the FTIR pump. The second bottle contained a 0.1 mol NaOH solution to clean the produced gas and prevent any oxygen going inside the reactor. The gas sampling vent was connected to the sampling probe to collect samples of gas every 20 s during the process. The FTIR analyser, the O₂ and H₂ analysers were turned on and left until their measuring cells reached 180 °C and 5 °C respectively. The FTIR analyser was calibrated manually using Calmet software. The main

pump was adjusted to 1.5 L/min, whereas the O₂ analyser pump was adjusted to 0.5 L/min.

Pre-treatment and Re-melting

The re-melting experiments were conducted mainly to investigate the metal yield and the coalescence efficiency. Different procedures and materials were tested to study the influence of organics (polymer coating and coffee residue) on metal yield and coalescence. Ceramic crucibles (Al₂O₃–SiO₂) were used for the experiments. A muffle furnace (Nabertherm HTCT 01/16) with a total volume of 1 litre, placed in a fume hood, was used for both pre-treatment and re-melting of the capsules.

Pre-treatment was performed in selected re-melting trials by heating up the capsules up to 500 °C and held for 30 min in air. Most of the organics were removed with this method and generated gasses were evacuated from the furnace. After pre-treatment, capsules became soft and were manually pressed together in the crucible to be able to cover the surface fully with the salt flux (NaCl). Subsequently, the crucible was heated up to 800 °C for the re-melting procedure. Some of the trials were performed without the pre-treatment to study its effect on the yield. In these experiments, the salt was added in the beginning of the trial and heated together with the capsules from room temperature. After reaching the final temperature, all melts were stirred for few seconds and left for solidification in the crucible. 25 capsules and 50 g of a 50–50 wt% NaCl:KCl mixture with 2 wt% CaF₂ was used in all remelting experiments. The recovered metal after each trial was removed by crushing the crucible and washing out the salt flux. The experimental matrix is shown in Table 1.

Results

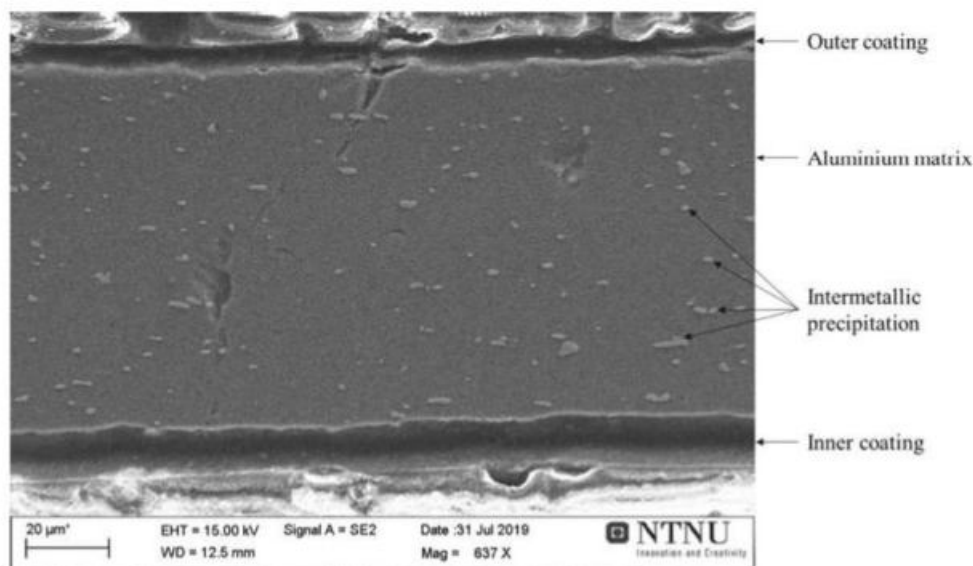
Starting Material Properties

The cross sections of coffee capsules were characterized in the SEM to measure the thickness of the coatings inside and outside of a capsule. A sectioned wall of a capsule is shown in Fig. 1. A pigment layer with optical purposes on the outer surface and a plastic coating to avoid contact between the coffee and the metal is found on the inner surface of each capsule. The total wall thickness was measured as 100 µm consisting of 13 µm of inner and 6 µm of outer coating. Intermetallic Al–Fe–Si precipitates are present in the matrix as seen in Fig. 1.

Six types of unused emptied (from coffee) capsules with different colours were heated in a resistance furnace up to 500 °C and held for 180 min to track the mass change due to burning of organics. Capsules were weighed before and after the heating and results are shown in Table 2. Mass of an empty unused capsule was found as 1.07 ± 0.01 g in

Table 1 Experimental matrix of pre-treatment and re-melting experiments

Trials	Condition of capsules	Pre-treatment at 500 °C for 30 min	Coffee residue	Remelting temperature (°C)
1–5	Used, mixed colours	Yes	No	800
6–7	Unused, yellow	Yes	No	800
8–9	Unused, green	Yes	No	800
10–11	Used, mixed colours	No	No	800
12–14	Used, mixed colours	No	Yes	800

Fig. 1 Cross sectioned wall of a coffee capsule

average and the capsules lost approximately 13% of their mass during the heat treatment.

A similar mass loss test was performed for used capsules containing coffee residue and water. Capsules were heated up to 500 °C and held for 0.5–4 h to find out the approximate duration necessary for complete removal of coffee residue and water. The results are shown in Table 3.

The trial with 2.5 h holding time was repeated 5 times to establish a confidence region and the final mass was 1.11 g in average with a standard deviation of 0.06 g. No significant change was observed after 2.5 h and the final mass was

slightly higher than the results with the clean capsules. The difference might be due to some ash retained in the capsules after burning the coffee residue, which was not the case for the clean capsules.

Figure 2 shows the mass distribution of components after a coffee capsule is used. The metal content of a capsule is 6.8 wt% which is equivalent to approximately 1 g metal per capsule. This metal proportion increases to 47 wt% after degradation of organics and removal of water.

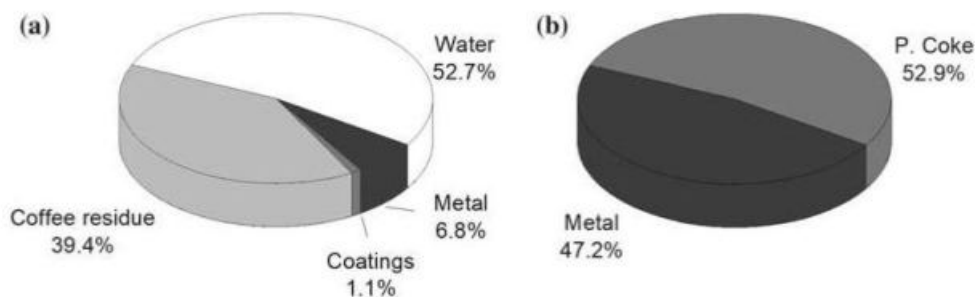
Furthermore, the colour change was observed before and after holding different capsules at 500 °C for 3 h. While the

Table 2 Mass loss after holding empty coffee capsules at 500 °C for 3 h

Colour of the capsule	Mass in grams (before)	Mass in grams (after)	Mass change %
Green	1.05	0.92	12.5
Black	1.07	0.93	12.7
Purple	1.07	0.92	13.9
Gold	1.06	0.92	12.8
Pink	1.08	0.94	12.9
Dark yellow	1.09	0.95	13.0

Table 3 Mass loss of used coffee capsules after heat treatment at 500 °C

Holding time at 500 °C	Mass in grams (before)	Mass in grams (after)	Mass change (%)
0.5	14.88	1.75	88.3
1	14.88	1.60	89.2
1.5	13.08	1.37	89.5
2	13.39	1.20	91.0
2.5	13.69	1.11 ± 0.06	91.9 ± 0.4
3	12.55	0.99	92.1
3.5	12.91	0.99	92.3
4	12.74	0.99	92.2

Fig. 2 Mass distribution of material components of a capsule before (a) and after pyrolysis (b)

shades of yellow did not change much in colour, darker coatings like blue, green and black can be removed completely with the heat treatment at 500 °C as seen in Fig. 3.

Pyrolysis Results

Degradation of organics during pyrolysis is a complex process. To define the exact formation of components can be challenging due to the multiple reactions that happen simultaneously. However, detection of main compounds in the off gas provides some hints about the degradation mechanism that can occur during the thermal process including drying, pyrolysis and melting. The cracking periods that happen during the pyrolysis process is identified in Fig. 4. During the whole process, at least two periods can be identified. The first one corresponds to a dehydration and the second to a degradation process. The organic material degrades into volatile components and char.

The first period—dehydration—is evidenced by the presence of H₂O in the produced gas at temperatures between 100 and 220 °C (Fig. 3d). The second period correspond to a strong cracking step, which degrades long organic molecules into short chain hydrocarbons like methane (CH₄), ethane (C₂H₆), ethylene (C₂H₄) and butane (C₄H₁₀) (Fig. 3a). In particular, cracking of aliphatics and aromatic bonds leads to formation of free hydrogen (H₂) and compounds from hydroxyl (–OH) group like cresols and acetic acid (CH₃COOH) (Fig. 3b, c). The last period corresponds to oxidation reactions (e.g. see Eqs. 1 and 2), resulting in formation of molecules like CO₂, CO and H₂O. Evidence of this degradation is clear at 300 °C, where water vapour is promoted as well as H₂, CO and CO₂. In addition, detection of ethane after 300 °C is stable until ~470 °C, where its formation is slowed down while formation of hydrogen and methane is favoured. The degradation of

Fig. 3 Different coffee capsules before and after holding at 500 °C for 3 h

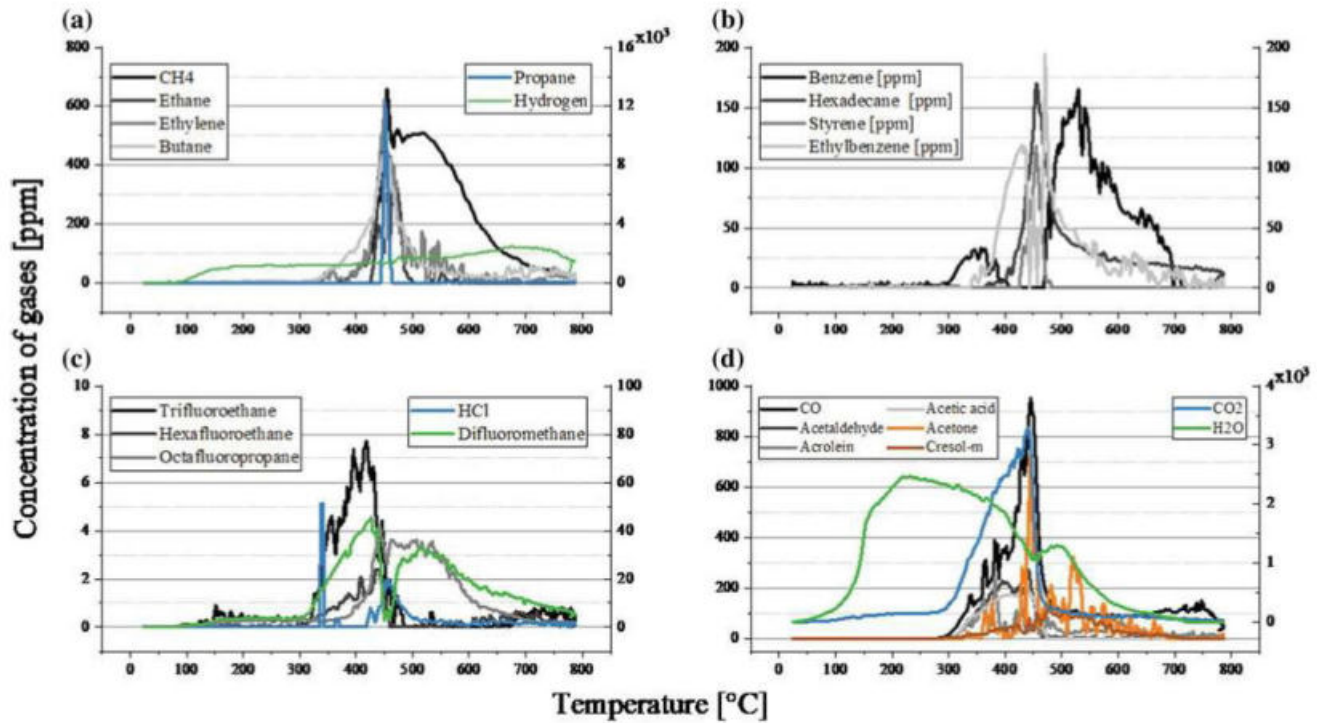


Fig. 4 Composition of generated gas during pyrolysis of used (wet and yellow type) capsules versus temperature: **a** permanent hydrocarbons and hydrogen, **b** condensable hydrocarbons, **c** halogenated compounds, **d** oxygen containing compounds

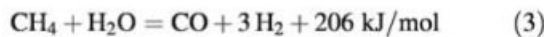
ethane in pyrolysis of organic containing materials has been already investigated in different studies. Ethane is firstly broken to two methyl radicals. A methyl radical forms the stable CH_4 molecule by hydrogen stripping from other ethyl molecule. In addition, The unstable ethyl molecule most probably break into methylene and free hydrogen [6, 7].

Combustion of hydrocarbons can be expressed as [8]:



Formation of hydrogen can be also expected in the so-called reverse methanation reaction, which promote formation of H_2 and CO , as indicated in Eq. 3. This can also explain the drastic drop in methane formation after 520 °C, while formation of hydrogen is promoted.

Reverse methanation reaction [8]:



In Fig. 4, the presence of condensable hydrocarbons like Benzene, hexadecane, Styrene and Ethylbenzene, that leads to formation of the so-called pyrolysis oil, is detected. As can be seen, their formation is more favourable above 400 °C due to secondary cracking of the tar formed at lower temperatures. This cracking process can also lead to increased formation of hydrocarbons like Benzene, Hexadecane,

Styrene and Ethylbenzene, but also short chain molecules like CH_4 , CO and H_2 .

From the off-gas analysis presented in Fig. 4, it can be also seen that formation of halogenated compounds are only stable in the gas phase after 300 °C. These compounds originate from the degradation of the epoxy resin in the plastic inner coating of the capsules. Therefore, formation of Trifluoroethane, Hexafluoroethane, HF, Octafluoropropane, Difluoromethane, HCl and C_5F_8 can only be detected above this temperature.

Remelting Results

The results of the re-melting experiments were evaluated by metal yield and coalescence efficiency. The yield and coalescence of each trial were assessed by using Eqs. 4 and 5 respectively. An efficient coalescence was defined as the coalescence of at least two capsules which will weigh at least 1.8 g (Table 2). Yield and coalescence results are summarized in Fig. 5.

$$\text{Metal Yield} = \frac{m_{\text{total recovered metal}}}{m_{\text{capsules charged}}} * 100 \quad (4)$$

$$\text{Coalescence Efficiency} = \frac{m_{\text{particles} > 2 \text{ grams}}}{m_{\text{total recovered metal}}} * 100 \quad (5)$$

Trials 1–11 were performed after emptying the coffee from the capsules. The pre-treated used mixed capsules showed

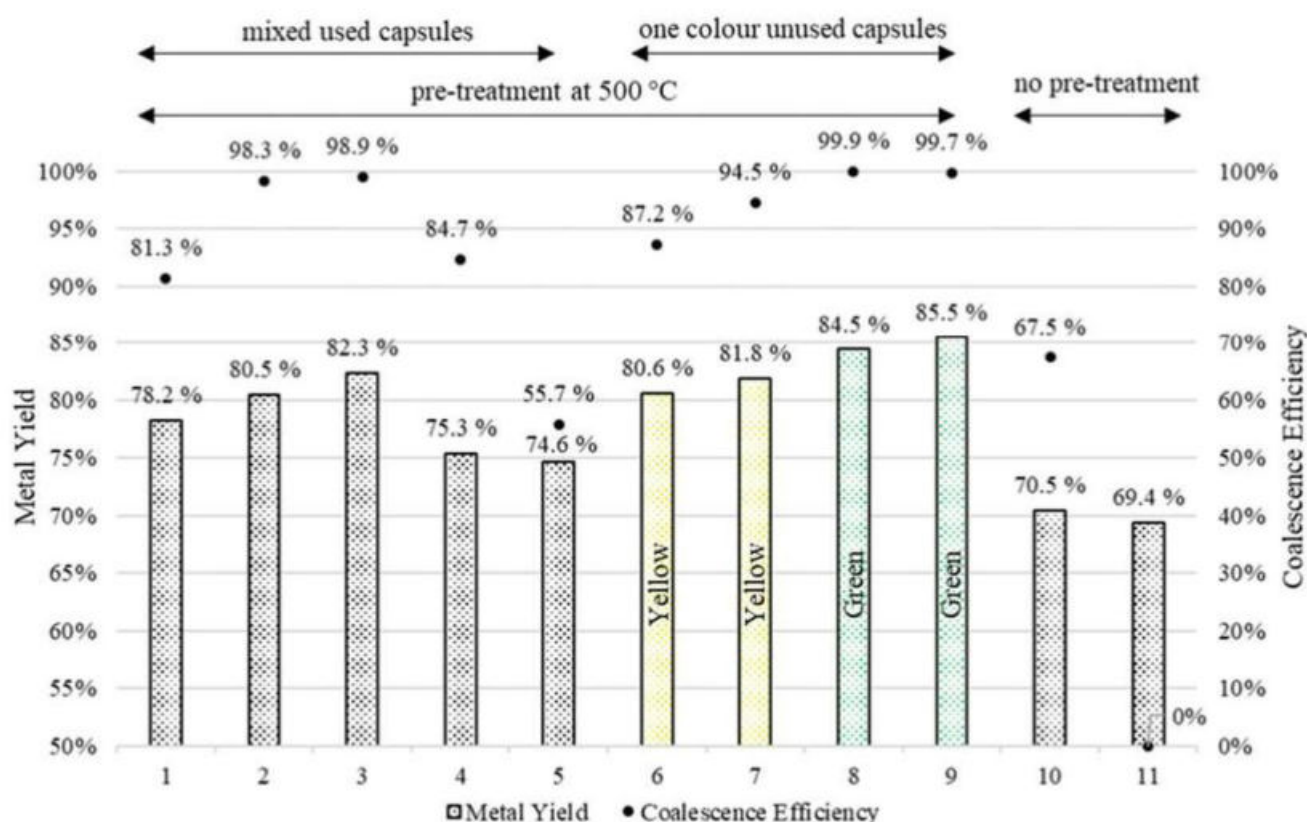


Fig. 5 Summary of metal yield and coalescence results after remelting of empty coffee capsules under a salt flux

metal yield results between 74.6 and 82.3% (78.2% in av.). The capsules heated from room temperature with a cover of salt flux (without pre-treatment) up to the pre-defined final temperature showed significantly lower yields of 69.4 and 70.5%. Furthermore, results of different coloured unused batches showed slightly different yields from each other. Metal yields of two parallels for yellow capsules were 80.6 and 81.8% and for green capsules 84.5 and 85.5%.

Coalescence efficiency varied from 0 to 100%. The efficiency was in average 83.8% for the used capsules (Trials 1–5) and 95.3% (Trials 6–9) for the unused ones, however the standard deviations were very high 18% and 6% respectively. One remelting trial without pre-treatment showed 67.5% (Trial 10) and an identical parallel, no coalescence (Trial 11). The effect of pre-treatment on coalescence behaviour is shown in Fig. 6. A spherical coalescence behaviour and shinier droplet surfaces were observed after remelting of pre-treated capsules. Conversely, coagulated metal after remelting of capsules without pre-treatment had rough surfaces, irregular shapes and darker colour due to oxidation.

Although coagulated drops looked similar in shape and colour after remelting pre-treated capsules, coalescence efficiency varied, as seen in Fig. 7.

Three additional remelting experiments were performed with capsules containing a coffee residue to investigate its behaviour during incineration (in case not returned to dedicated collection points). The results are shown in Table 4. The yield decreased drastically due to the presence of coffee residue and the efficiency further decreased with increasing amount of the coffee. Flames were clearly observed during heating.

Two samples from the recovered metal from the coffee capsules was analysed by ICP-MS. The results are shown in Table 5. The results from trial 1 to 3 showed a purity of 98.95% and 98.98% respectively. The main alloying elements (Fe and Si) did not vary significantly between trials, as expected.

Discussion

Capsules with different colours (coatings) showed different metal yields during re-melting. Although inner coatings behave the same (same polymer coating in every capsule), the outer coating behaviour is different from capsule to capsule, as seen in Fig. 3. Obviously, the behaviour of the coatings plays a role in oxidation during remelting. The heat treatment of samples with different colours showed that

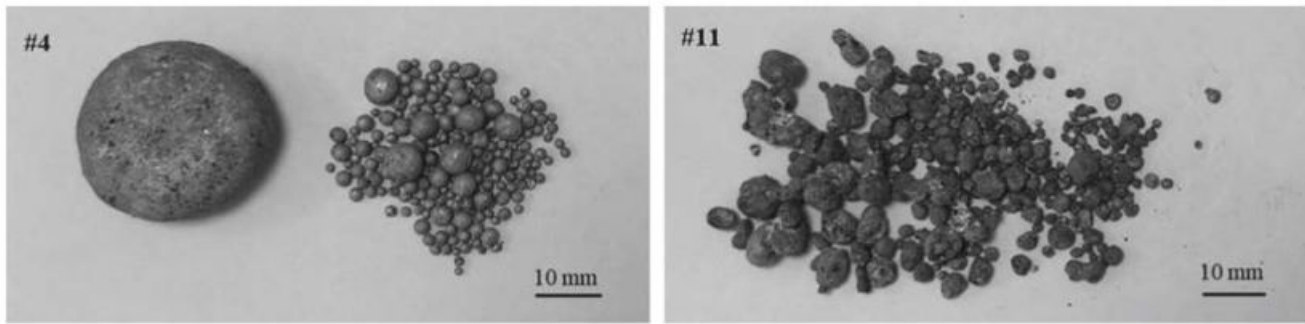


Fig. 6 Coalescence behaviour of capsules with and without pre-treatment prior to melting

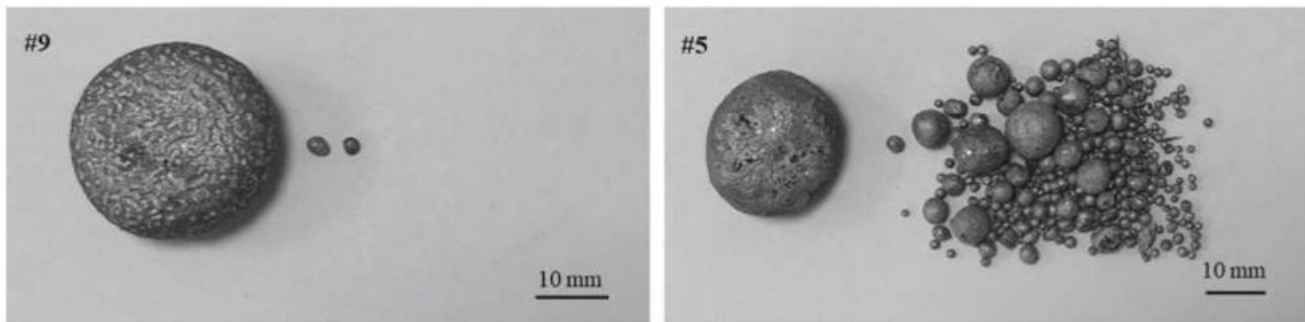


Fig. 7 Different coalescence behaviour of capsules remelted after a pre-treatment

Table 4 Summary of metal yield results after remelting used capsules with coffee residue

Trial	Amount of residual coffee in the capsule volume (%)	Total organic content (%)	Metal yield (%)
12	10	43.6	10.2
13	50	77.0	2.9
14	100	86.2	0

Table 5 Elemental composition of recycled metal

Element	Trial 1 (ppm)	Trial 3 (ppm)	Element	Trial 1 (ppm)	Trial 3 (ppm)	Element	Trial 1 (ppm)	Trial 3 (ppm)
Fe	7080	7140	Ti	194	166	Ca	26.8	24.6
Si	1380	1170	Cr	14.5	21.9	Mo	5.0	6.9
Cu	225	410	Ni	41.6	47.8	Na	679	550
Mn	409	353	Pb	12.5	12.6	K	89.1	56.2
Mg	18.2	22.5	Cd	0.1	0.1	S	<40	<40
Zn	232	160	Sn	2.1	3.1	P	3.0	4.3

coatings behave differently from each other and that the yellow/gold shade capsules cannot be de-coated at typical pre-treatment temperatures in recycling. In other words, the de-coating process will be completed only during re-melting. The late decoating tendency of yellow colours affected the yield negatively during the remelting procedure.

Re-melting of used emptied (from coffee) capsules generated significantly lower metal yields than the new ones. It

is known that every capsule has approximately 13% organics from the coating materials, which burns mostly before re-melting occurs. Therefore, the yield below 87% corresponds to the oxidation during storage of the wet capsules and during the remelting process. Both oxidation mechanisms can be possible due to the promotive effect of water vapor on oxidation, as indicated in the results from pyrolysis experiments with integrated off-gas analysis. Presence of

water in spent coffee capsules represent an important challenge to the process. Water vapour is initially liberated due to trapped water in the coffee residue after 100 °C. In addition, H₂O is also produced as a reaction product from the combustion process of polymers, which occurs even in complete absence of atmospheric oxygen. This can be explained due to the presence of hydroxyl radicals in the compounds generated during the pyrolysis itself like cresols and acetic acid. It should be noted that water formation during degradation of organics, might lead to undesired oxidations reactions with aluminium as indicated in Eqs. 6–8 [9]. From the off-gas analysis, the presence of hydrocarbons in both condensable (Benzene, Hexadecane, Styrene and Ethylbenzene) and permanent forms (CH₄, Ethane, Ethylene, Propane, Butane) in addition to considerable amount of CO₂, CO, hydrogen and some halogenated compounds, is identified. These compounds have to be handled properly in the recycling process off-gas treatment system with both proper post-composition and halogen remediation. It is to be expected that at industrial conditions, increased presence of oxygen in the system leads to increased combustion reactions, thus, increased generation of water vapor.

Aluminium oxidation with H₂O [9]:



Re-melting with coffee residue in the capsules dropped the yield drastically. Metal yield dropped to zero after remelting of used capsules with full coffee residue, corresponding to approximately 86% of total organics. The burning of high amounts of organics generates a very oxidative atmosphere and a very long duration of gas generation. Usually an organic content over 5% is not recommended in furnace charges without a pre-treatment in aluminium recycling [10].

Different coalescence efficiencies were observed during the re-melting process of different trials however, it is not possible to draw a conclusion since coalescence is an operation-related phenomenon. In aluminium recycling industries, old scraps are remelted under a salt flux in rotary furnaces to optimize the interaction between the salt and the metal as well as promote the coalescence [11]. The presented results were obtained in a laboratory resistance crucible furnace and the coalescence was mostly controlled by a mechanical stirring prior to solidification which can differ in each trial.

Conclusions

The recyclability of used coffee capsules was investigated in terms of metal yield. Effects of thermal pre-treatment and organic content were investigated experimentally as well as an off-gas analysis during heating. The results of the investigation showed that:

- Organic matter in aluminium containing items can be a challenge in the recycling process. Coffee capsules contains 86 wt% coffee and other organic (coatings) materials, which will degrade into volatile gases and pyrolytic coke during thermal treatment. The degradation of organics has an important influence on the metal yield since produced gases react with aluminium to produce aluminium oxide, which cannot be recovered during the remelting in salt. Future work should investigate the effect of oxygen in the thermal pre-treatment process as well as the effect of heating rate.
- Water vapor seems to have the largest impact on the metal yield, as considerable amount of water is contained in the coffee in the spent capsules and additionally generated from combustion reactions of organic (polymer coating and coffee residue) content. Therefore, spent coffee capsules should be shredded before thermal pre-treatment to separate coffee residue and capsules.

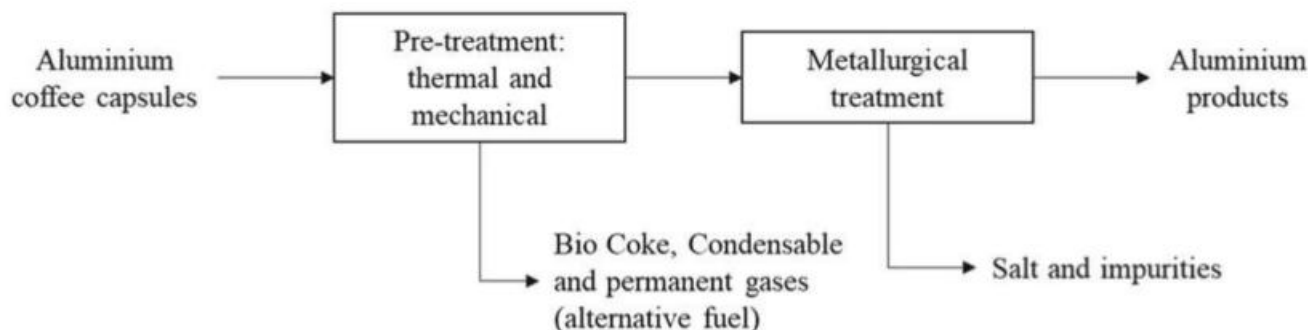


Fig. 8 Proposed recycling concept for spent coffee capsules

After thermal and mechanical pre-treatment, direct re-melting can be applied to recover the metal content of the capsules. The proposed recycling concept is presented in Fig. 8.

- The remelted aluminium had the purity of ~99 wt% Al. Main minor/alloying elements are Fe and Si. Na and K concentrations are high due to the recycling process under a chloride based salt flux which can be removed by fluxing with either pure chlorine or chlorine/inert gas mixtures.

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