Life Cycle Assessment and Comparison of Magnesium Oxide Nanoparticles Prepared by Aqueous and Microwave Synthesis Methods

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Abstract

Abstract: Magnesium oxide nanoparticles are being used increasingly as catalysts for organic synthesis, fuel oil additives, and CO_2 adsorbents. There are many ways to produce magnesium oxide nanoparticles, but there is little information available regarding the environmental costs of production. As demand for environmentally friendly materials increases, it is important to understand environmental impact differences between various production methods. This study will compare the differences in embodied energy and global warming potential (GWP) between two synthesis methods: microwave combustion synthesis (microwave synthesis) and oxidation of magnesium hydroxide (aqueous synthesis). The resulting nanoparticles were characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM) and energy dispersive X-ray spectrometry (EDS). Nanoparticles produced through microwave synthesis formed nanocubes while aqueous synthesis produced round particles with less pronounced facets. The embodied energy and GWP were determined using life cycle assessment (LCA), and it was found that the embodied energy and GWP of magnesium oxide nanoparticles produced by microwave synthesis were significantly less than that of aqueous synthesis.

1. Introduction

Magnesium oxide (MgO) is a readily available material that has numerous applications as an electrical insulator, thermal insulator, substrate, catalyst[1], and CO_2 adsorber[2]. MgO nanoparticles have greater utility as catalysts than bulk materials or microparticles due to their increased specific surface area. Applications that rely on high surface area MgO particles include CO_2 capture, catalysis of organic reactions, and filtration. MgO nanoparticles are also receiving attention as a fuel oil additive that increases fuel efficiency, reduces NO_x emissions, and reduces sludge buildup within engines[3]. Magnesium is the eighth most abundant element in the earth's crust and is currently extracted from salt water.

There are two main approaches to producing MgO nanoparticles: combusting magnesium in oxygen, and calcining magnesium hydroxide particles. This study looks into one method from each approach. The first method is to combust magnesium metal in oxygen. This results in the production of a great amount of heat and light, and produces MgO nanocubes. The particular

method in this study has previously been investigated as a way of producing pure, ready-to use nanocubes[4].

The second approach is a chemical synthesis method starting with the formation of magnesium hydroxide precipitates in an aqueous solution. The magnesium hydroxide is then dried and oxidized in a furnace[5]. In this approach, the rate of reaction can be controlled to a much higher degree by altering the concentration of reactants and oxidation temperature. The particle size of the resulting MgO nanoparticles is affected by the concentration of the reactants in the aqueous step.

2. Experimental Procedure

2.1 Microwave Synthesis

In the microwave synthesis method the objective is to vaporize and combust magnesium metal by arcing steel wool mixed with magnesium to produce a MgO vapor that will condense on a silica substrate. 30 mg of steel wool was gathered into a ball and placed inside an alumina crucible. 30 mg of magnesium ribbon was sliced lengthwise to produce thin, wire-like magnesium ribbons, then placed in the crucible with the steel wool and lightly mixed. The crucible was then covered by a glass microscope slide and a crucible lid. The crucible, slide, and lid assembly (Figure 1) were then placed inside a glass bowl within a household 1000 Watt microwave (Magic Chef model HMD1110B).
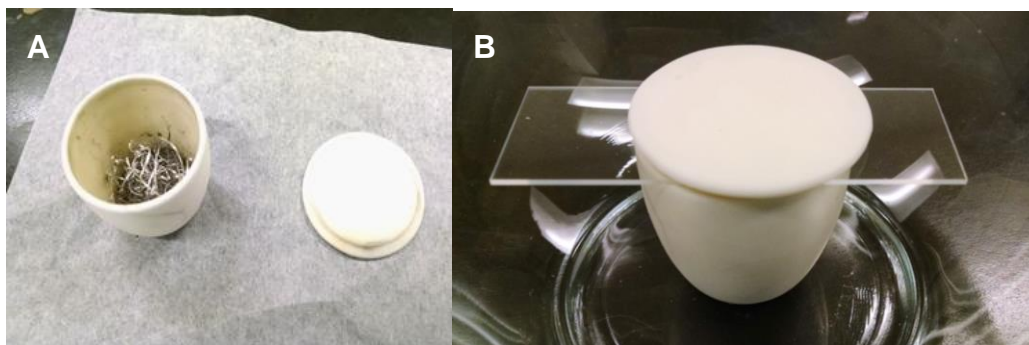

Figure 1. The alumina crucible containing 30 mg of shredded magnesium ribbon and 30 mg of steel wool (A). Filled crucible covered with glass microscope slide and alumina lid (B).

The microwave was set for 1000 Watts and turned on for 30 seconds. The magnesium and steel wool react in bursts as the material arcs and burns. The material in the crucible has typically completed reacting before the microwave turns off. After allowing the crucible to cool for 20 minutes, it is removed from the microwave. A clearly visible white MgO powder is deposited on the microscope slide where it covered the crucible (Figure 2). The mass of the slide with powder was compared to the mass of the slide before the process to determine the mass of powder produced, which was 16 milligrams. The slide with MgO particles was then stored in a slide case for further analysis.

2.2 Aqueous Synthesis

Reactant solutions of magnesium nitrate and sodium hydroxide were prepared such that mixing equal volumes of solution would result in the stoichiometrically ideal balance of reacting ions. 0.1 M magnesium nitrate solution was prepared by dissolving 1.483 g of magnesium nitrate in 100 mL of deionized water in a 250 mL glass beaker. 0.2 M sodium hydroxide solution was prepared by dissolving 0.799 g of sodium hydroxide in 100 mL of water. The sodium hydroxide solution was then mixed into the magnesium nitrate solution under constant stirring on a magnetic stir plate. The mixture of magnesium nitrate and sodium hydroxide was left on the stir plate for 2 hours to react. The sodium hydroxide reduced the magnesium nitrate to form magnesium hydroxide precipitates and sodium nitrate in solution. After 2 hours, stirring was ceased and the magnesium hydroxide precipitates were allowed to settle at the bottom of the beaker (Figure 3).
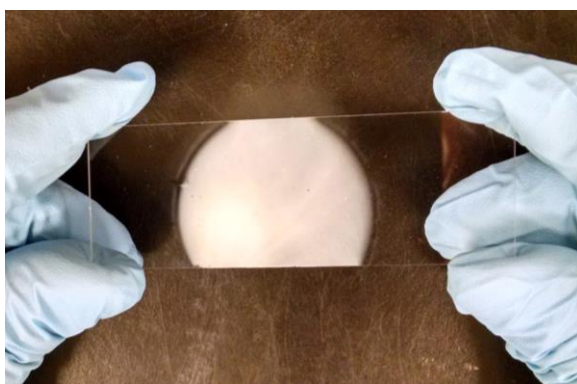

Figure 2. MgO produced in the microwave is deposited on the underside of a glass microscope slide.
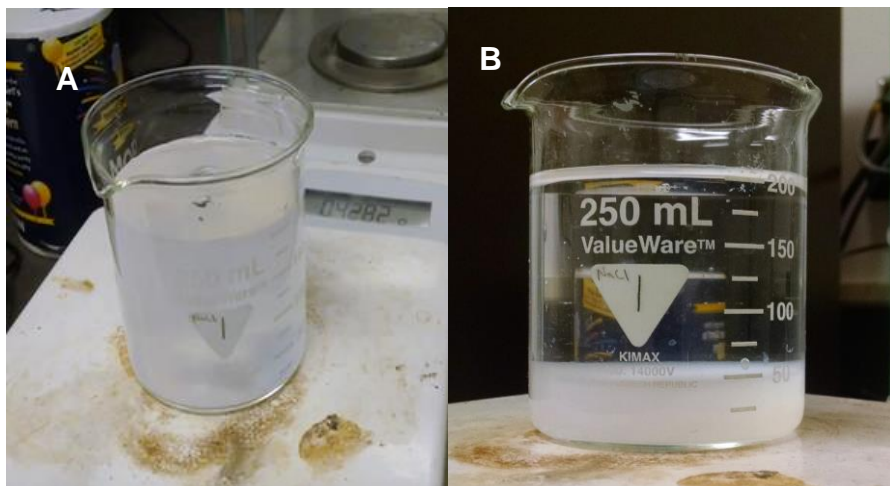
Figure 3. (A) Magnesium nitrate and sodium hydroxide mixing on a stir plate. (B) Cloudy white magnesium hydroxide precipitate settles to the bottom of the aqueous solution.

Once settled, the supernatant was removed and ~50 mL of ethanol was added to it in a washing step. The suspension was then left to settle overnight after which the washing step of removing the supernatant was removed and adding ~50 mL of ethanol was repeated. After letting the precipitate settle overnight once again, the supernatant was removed and the suspension was left uncovered under a laminar flow hood for approximately 8 hours. After approximately half of the remaining solvent had evaporated, the sample was placed in a Fisher Scientific Isotemp™ Oven at 110ºC for 12 hours to remove any remaining solvent (Figure 4).

Figure 4. Dry magnesium hydroxide on the bottom of the beaker after oven drying.

After being removed from the oven, the magnesium hydroxide was transferred from the beaker to a small alumina crucible for calcination. Calcination of the magnesium hydroxide was carried out in a Fisher Scientific Isotemp™ Muffle Furnace at 500ºC for 4 hours. The crucible was then removed and allowed to air cool to room temperature (Figure 5). At this point the process for producing MgO nanoparticles was complete and the sample was weighed and transferred to a plastic test tube for later analysis. 0.2601 grams of MgO nanoparticles was produced using this method.

Figure 5. The MgO clumps together in flakes. Agitation of the flakes breaks them up into a fine powder.

2.3 Characterization

2.3.1 SEM

To determine the structure of the materials produced, they were first examined using a scanning electron microscope (SEM). The samples were not sputtered with conductive metal, but left in their as-synthesized condition. For both microwave and aqueous samples, an adhesive copper tape was contacted to the powder and placed on an electrically conductive SEM sample holder. Secondary electron SEM images were taken of the coated surface of the glass slides used in the microwave process. This method was unable to produce SEM images in which the particle features were visible, although it did show the presence of small particles, 2 microns in size or smaller resulting from microwave synthesis (Figure 6).
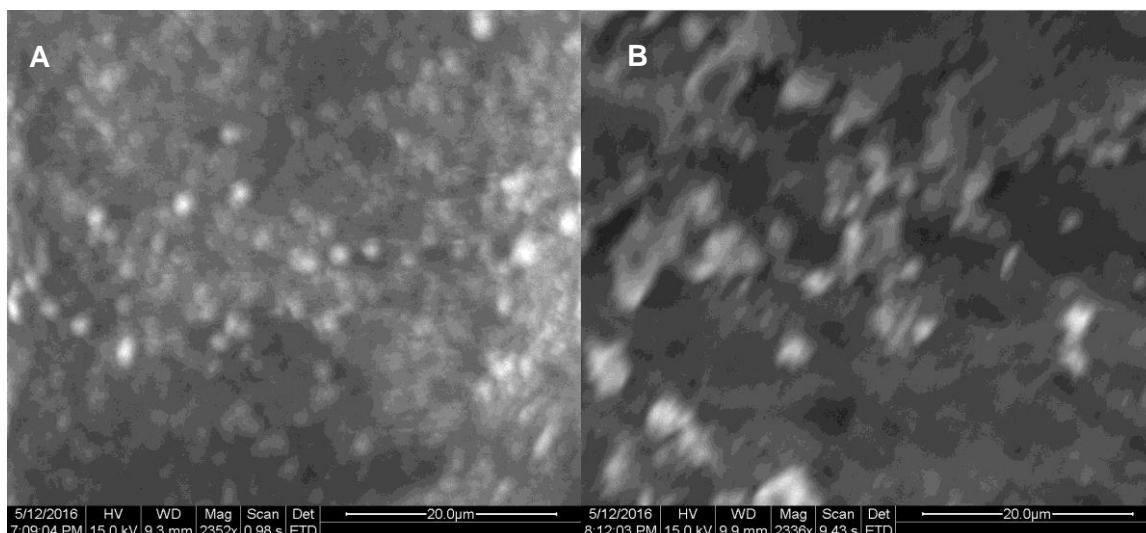
Figure 6. SEM images of MgO produced by (A) microwave synthesis and (B) aqueous synthesis.

2.3.2 TEM and EDS

Because of the small size of the nanoparticles being produced and their non-conductive nature, the samples were imaged using the Philips CM200 transmission electron microscope (TEM) at Lawrence Berkeley National Laboratory. MgO nanoparticles were dusted onto Formvar-coated copper TEM grids for analysis. Energy dispersive x-ray spectrometry (EDS) was also performed with this TEM to determine the composition of the produced material.

2.4 Life Cycle Assessment

Life cycle assessment (LCA) is a technique used to evaluate the environmental impact of a given process or product. For products, life cycle assessment generally consists of 5 different phases: materials, manufacturing, transportation, use, and end of life. LCA usually looks at one or more impact categories, such as embodied energy, toxicity, and global warming potential (GWP). GWP is a relative measure of how much of an impact a greenhouse gas has on the environment. GWP is measured in kilograms of CO_2 equivalent produced per kilogram of product. The goal of this LCA was to find the embodied energy and GWP of the MgO nanoparticles produced via each of the microwave and aqueous methods. The LCA performed for this project includes the materials and processes (manufacturing) used to produce the MgO nanoparticles. This LCA does not explore the transportation, use, or end of life of the MgO nanoparticles. This LCA also does not include the embodied energy or GWP of the stir plate, microwave, oven, or furnace used in

the synthesis methods, as the embodied energy and GWP data for these items could not be reliably obtained.

In conducting the LCA, material and energy flows for each synthesis method were closely tracked. Material inputs were measured by their consumption in grams. The power consumption of the microwave and stir plate were measured using an Extech PQ2071 AC Clamp Meter. The power consumption of the oven and muffle furnace were estimated based on their power ratings. Emissions due to electricity usage, 0.2074 kg CO_2/kW-h, was based on the PG&E's 2009-2013 emissions average. CO_2 equivalence for other greenhouse gases was based on the IPCC Fifth Assessment Report[6]. The embodied energy and GWP were obtained using CES Edupack 2015 software unless otherwise stated. The values of embodied energies and flows are shown in Table 1.

Table 1. Material Embodied Energies and Global Warming Potentials for MgO Nanoparticle Synthesis

Materials	Embodied Energy (MJ/kg MgO)	GWP (kg/kg MgO)
Magnesium[7] *	187.95 - 211.11	25 - 47
Steel Wool	62.2 - 68.6	5.78 - 8.19
Alumina	49.5 - 54.7	7.080 - 7.837
Silica	2.25 - 2.49	7.080 - 7.837
Primary Production Cellulose	49 - 54	3.092 - 3.420
Ethanol[8] **	4.816	0.277†
Nitric Acid[9]	6.000 - 9.267	2.065
Magnesium Nitrate ***	35.902 - 42.474	5.852 - 9.458
Sodium Hydroxide[10]	3.5	0.633
Water[11] ****	0.011359	0.000654†

† When GWP was not given for a material, an approximation was calculated using embodied energy and PG&E's 2009-2013 GHG emission averages.
* Embodied energy totaled from burning of fuels and electricity usage.
** Values converted from BTU and gallons.
*** Embodied energy and GWP calculated from values for magnesium and nitric acid using stoichiometric ratios.
**** Converted from GJ/mega gallon.

3. Experimental Results

3.1 Microwave Synthesis Results

3.1.1 TEM

The TEM images of the MgO particles were much more revealing than the SEM images. The particles produced by microwave synthesis took the form of nanocubes in the same manner of magnesium smoke particles (Figure 7).
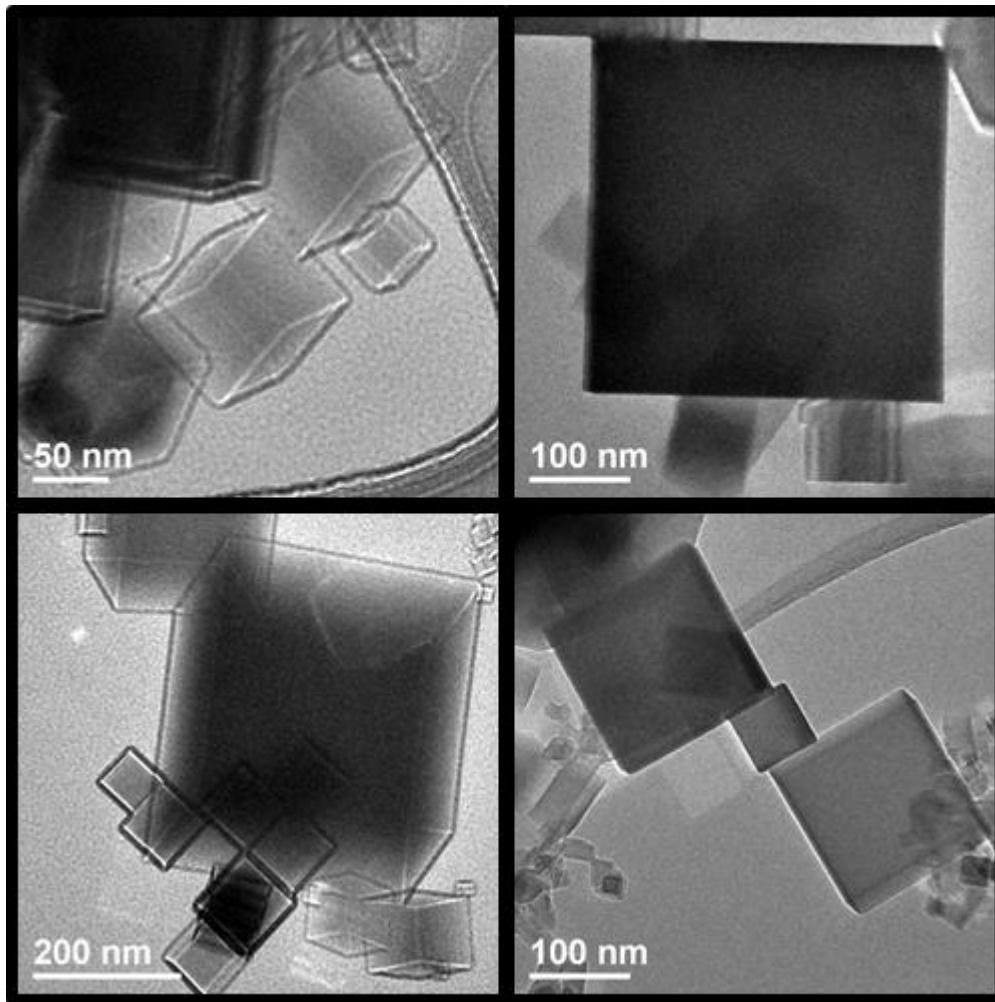

Figure 7. TEM images of MgO nanocubes and microparticles produced by microwave synthesis. (TEM images courtesy of Prof. Jean Lee)

Not all of the particles produced in microwave synthesis are nanoparticles. Some of the particles had characteristic dimensions of greater than 100 nm. However, this method also produced particles smaller than 25 nm.

3.1.2 EDS

EDS results show that the MgO particles produced by microwave synthesis are of high purity. The EDS spectrum shows that magnesium, oxygen, and copper were the only elements detected in the microwave samples (Figure 8). The copper detected by EDS likely comes from the copper grid that the sample is mounted on for TEM.
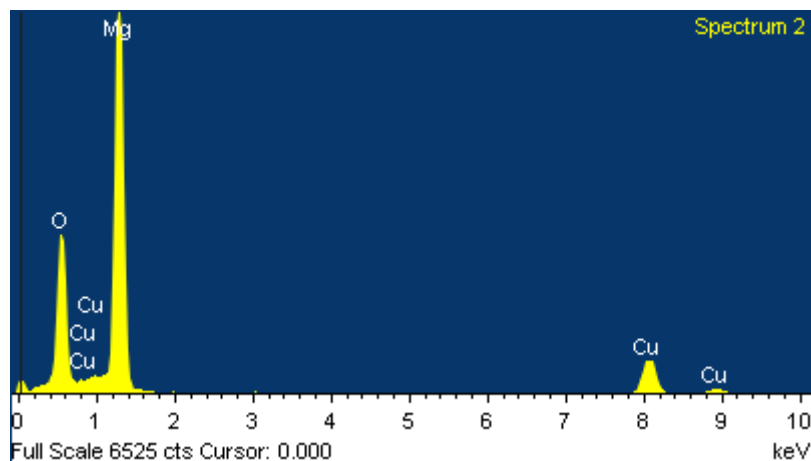

Figure 8. MgO nanoparticles produced by the microwave synthesis method exhibit clear peaks for magnesium and oxygen. Copper peaks are present that are likely due to the copper TEM grid. (EDS data courtesy of Prof. Jean Lee)

None of the iron or alloying elements from the steel wool were detected in the MgO particles. It is possible that when the steel wool combusts, it immediately forms an ash that settles on the bottom of the crucible rather than becoming dispersed in air.

Table 2 shows the quantitative composition results from EDS for particles produced using the microwave synthesis method. The ratio of oxygen to magnesium is nearly 1:1 in terms of atomic percent. From this data it can be concluded that the particles are made of high purity MgO.

3.2 Aqueous Synthesis Results

3.2.1 TEM

The TEM micrographs revealed that the particles produced by the aqueous synthesis method were morphologically different than those produced by the microwave synthesis method (Figure

9). While particles produced by microwave synthesis were cubes with a wide range of sizes, the particles produced by aqueous synthesis tended to be round and between 50 and 100 nm.

Table 2. Composition of MgO Nanoparticles Produced by Microwave Synthesis

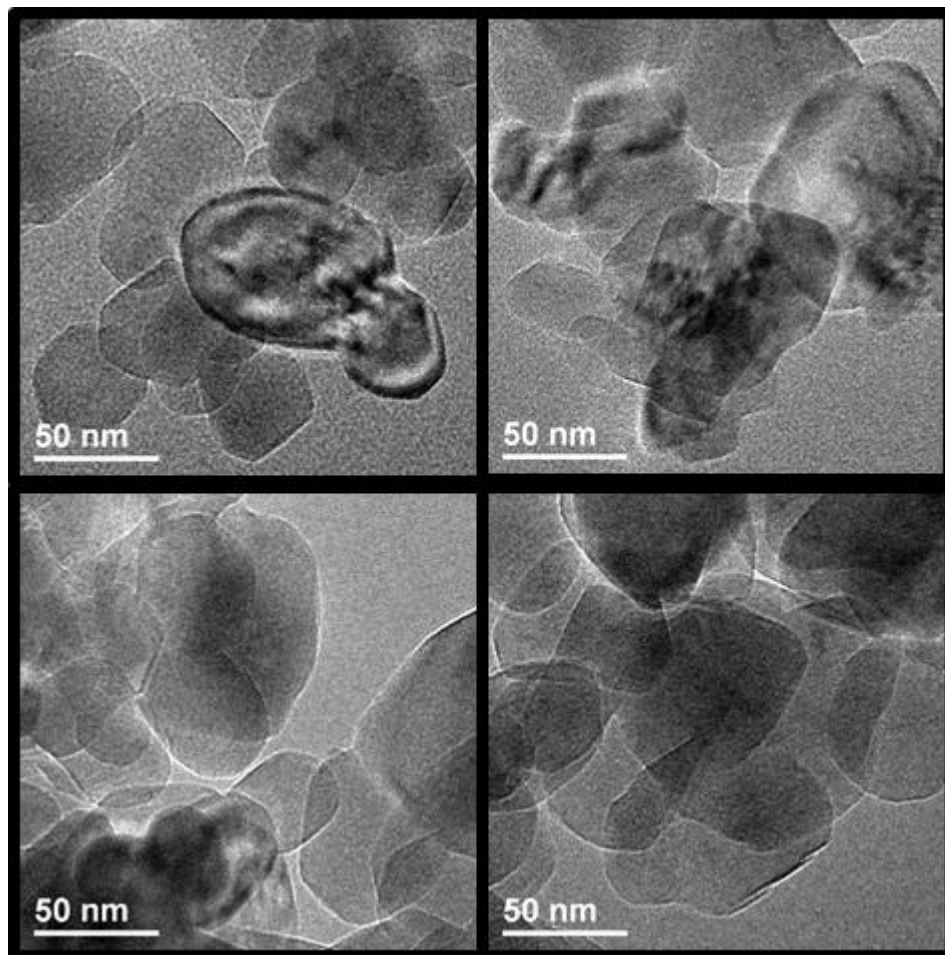| Element	Weight %	Atomic %
O	34.53	47.08
Mg	54.98	49.32
Cu	10.48	3.6
Totals	100	100

Figure 9. MgO nanoparticles produced by aqueous synthesis. The particles are rounder in shape than those produced by microwave synthesis, but still appear to be crystalline, having some flat facets. (TEM images courtesy of Prof. Jean Lee)

3.2.2 EDS

The EDS spectrum from the MgO synthesized by the aqueous method shows oxygen, carbon, and silicon in addition to the expected magnesium and oxygen (Figure 10). As with the previous EDS results, it is likely that the copper is present due to the TEM grid. Carbon is likely present from the thin Formvar film coating the TEM grid. The small silicon peak is likely from the EDS detector.
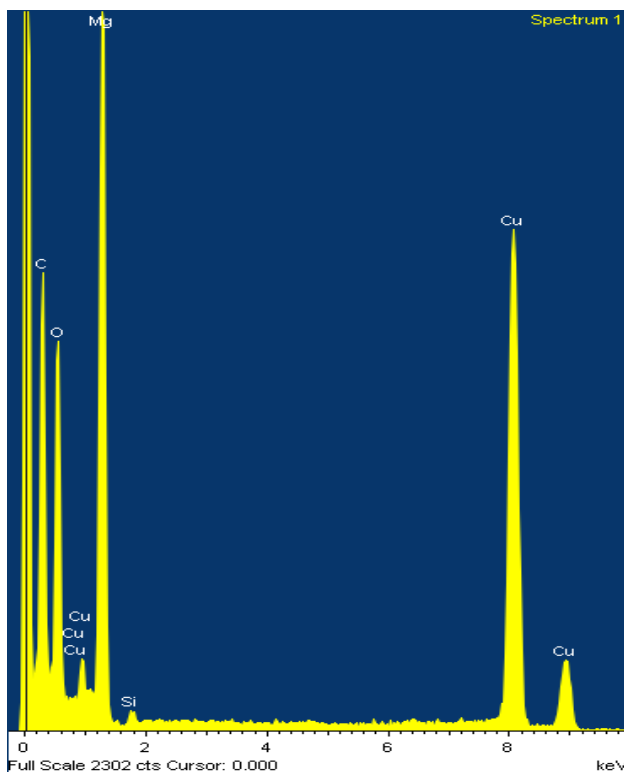

Figure 10. EDS spectrum of MgO nanoparticles produced by aqueous synthesis. (EDS data courtesy of Prof. Jean Lee)

The composition of the nanoparticles was given in terms of weight percent (Table 3). The relative quantities of oxygen and magnesium are compared to each other in Table 4. Pure MgO is 38.8 weight % oxygen and 61.2 weight % magnesium, suggesting that the MgO particles produced by the aqueous method is oxygen-rich. This excess oxygen may be due to the presence of residual magnesium hydroxide and / or the oxygen in the Formvar film.

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Table 3. Composition of MgO Nanoparticles Produced by Aqueous Synthesis

Element	Weight %	Atomic %
C	30	50.0
O	18	22.5
Mg	21	17.3
Si	1	0.7
Cu	30	9.5
Totals	100	100

Table 4. Relative Amounts of Oxygen and Magnesium in Nanoparticles Produced by Aqueous Synthesis

Element	Weight %	Atomic %
O	46.2	56.6
Mg	53.8	43.4

3.3 Life Cycle Assessment Results

Once the material flows were measured, the energy inputs from materials were calculated by multiplying the mass of each material used for synthesis with its embodied energy and adding up the results. This sum was then added to the measured or estimated values for power consumption to get the total energy input for the process. This total energy was then divided by the mass of MgO produced to estimate the embodied energy of the nanoparticles produced. The process was then repeated with GWP in place of embodied energy to find the GWP of the produced MgO nanoparticles. The results of the LCA can be seen in Figure 11.

The aqueous synthesis approach produces MgO nanoparticles with over ten times the embodied energy and GWP of those produced by microwave synthesis. The reason for the disparity becomes clear upon examination of the energy and GWP contributions by source for each method (Figures 12, 13, 14, and 15).

For the microwave synthesis method, the biggest source of embodied energy was the cleaning supplies. The major contributor in this category was cellulose Kimwipes used to clean the crucible and other tools. The contribution of the Kimwipes is large because for every 15-17 mg of MgO nanoparticles produced, about 3 grams of primary production cellulose in the form of Kimwipes was used for cleaning equipment and tools.
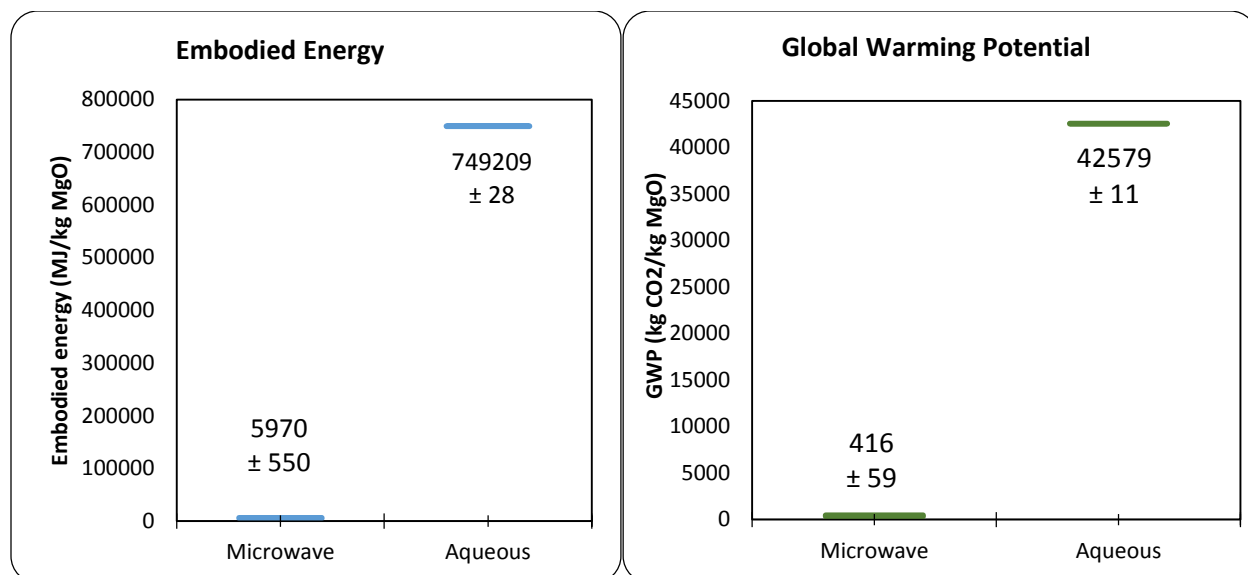
Figure 11. LCA results showing embodied energy and GWP for each of the microwave and aqueous methods of synthesizing MgO.

For the aqueous synthesis method, the electricity used in the stir plate, oven, and furnace makes up the biggest embodied energy contribution. This is due to the fact the oven and furnace are run at high temperatures for a long amount of time, and only about 0.26 grams of MgO were produced using equipment made for heat treating macroscale samples. The same trends observed with the embodied energy for each of the two synthesis methods can be seen with their GWPs (Figure 13).

4. Discussion

4.1 Environmental Implications

This study suggests that the microwave method for producing MgO nanoparticles used less energy and has a lower GWP than the aqueous synthesis method, but there are other environmental factors that were not taken into account. If the processes were optimized and the quantity of material being processed was increased, there would likely be a dramatic decrease in embodied energy and GWP for both methods. None of the equipment in this study was used anywhere near full capacity save for the stir plate in the aqueous synthesis method. In addition to GHG emissions, other forms of waste should be considered. Microwave synthesis produces solid waste in the form of iron oxide and MgO ash while aqueous synthesis produces a solution of sodium nitrate. Due to the lengthy high temperature heat treatments required for the aqueous

synthesis method, the microwave synthesis method (or possibly another combustion synthesis method) would likely be the more environmentally friendly option.
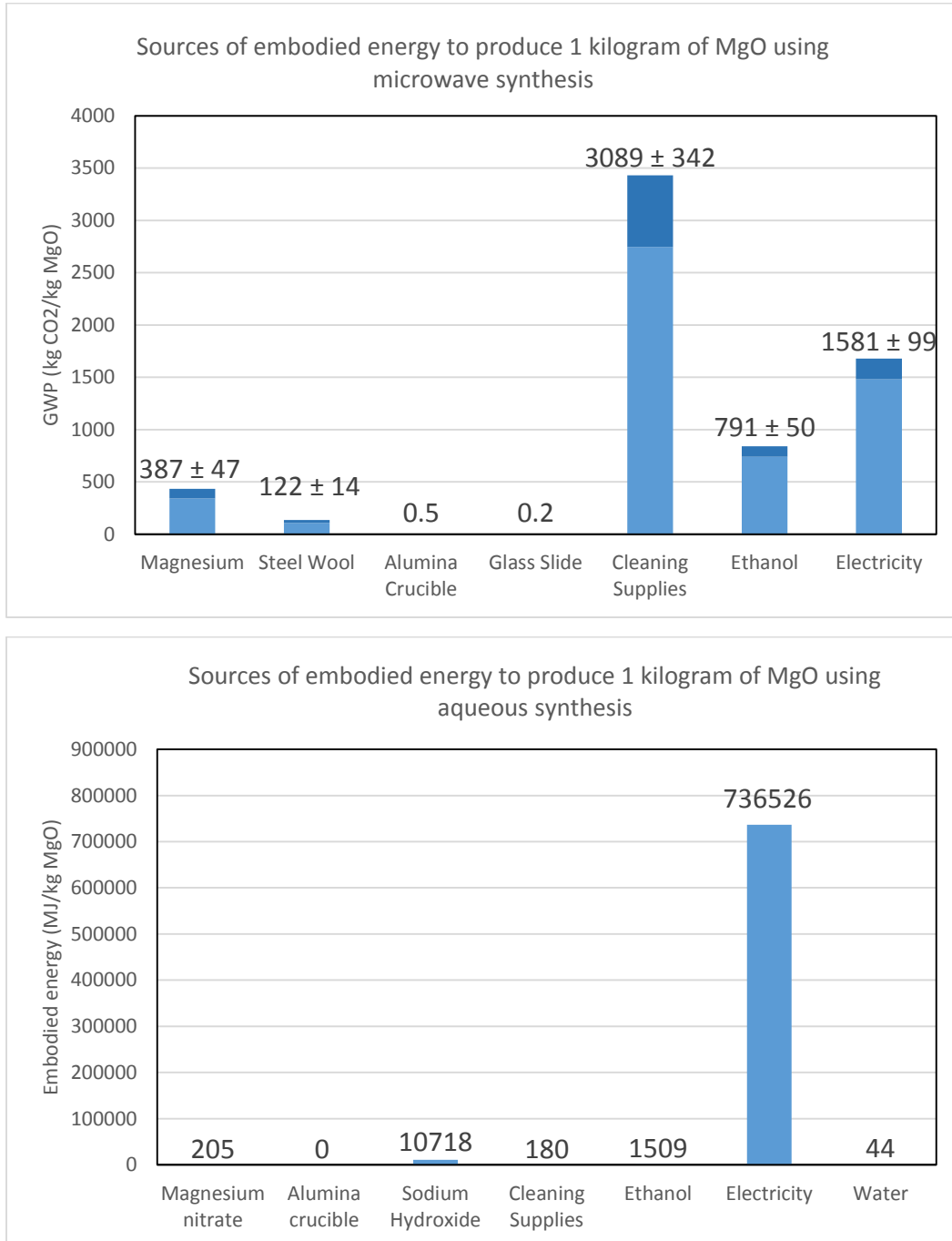

Figure 12. Breakdown of contributions to the embodied energy associated with the microwave synthesis method (top) and the aqueous synthesis method (bottom). The darker shaded regions show the range of embodied energy contributions.
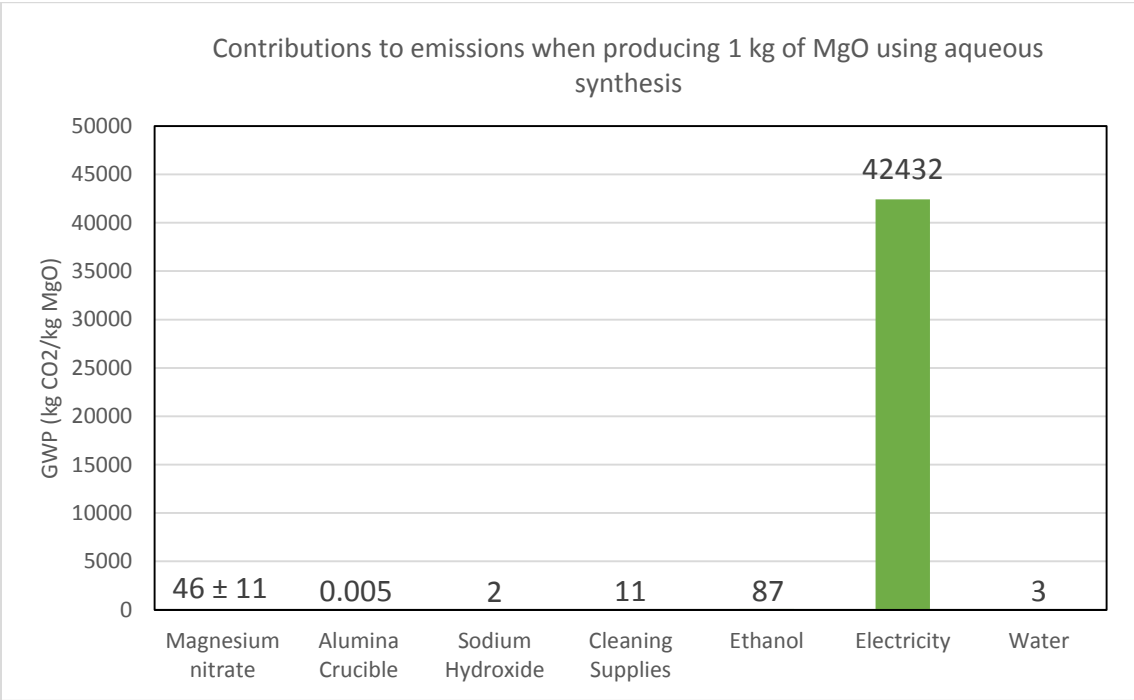
Figure 13. Breakdown of contributions to the GWP associated with the microwave synthesis method (top) and the aqueous synthesis method (bottom). The lighter-shaded regions span the range of GWP contributions.

4.2 Structure of Produced MgO Nanoparticles

Microwave synthesis produced nanocubes with a wide range of sizes and what are likely to be {100} facets corresponding to the Wulff construction for MgO nanoparticles. Aqueous synthesis, on the other hand, produced rounder nanoparticles of more consistent size and shape. The difference in shape may be due to a variety of factors. The shape of the MgO nanoparticles produced by the aqueous synthesis method is likely due to the diffusion of surface atoms resulting from the MgO particles being heated at an elevated temperature for a longer time in the furnace in comparison to the microwave synthesis method. As temperature increases, the differences in the surface energies of various crystalline planes can decrease, leading the equilibrium shape to be more spherical, rather than favoring only the lowest energy surfaces[12]. The structure could also relate to how magnesium hydroxide precipitates out of aqueous solution. It is possible that after calcination, the shape of the particles doesn't substantially change when the material is converted from magnesium hydroxide to MgO as both materials are solids and rely on diffusion to change shape.

4.3 Uncertainty in Data and Results

Neither synthesis process was optimized for efficiency. This may skew the results in favor of the process that just happened to be more efficient. The processes studied were likely created for laboratory study and for obtaining quick results. While this study encompasses the energy and materials used to produce MgO nanoparticles using these two methods, some of the equipment used were not included in the LCA. This was due to the difficulty in finding reliable estimates for their embodied energy and GWP. The equipment that was not included are the microwave, the stir plate, the oven, and a muffle furnace. Because the microwave is the only item missing from the microwave synthesis LCA in contrast to much of the equipment not being included in the aqueous synthesis LCA, the addition of the missing equipment to the LCAs is expected to have a greater impact on the embodied energy and GWP of MgO nanoparticles produced via aqueous synthesis. On the other hand, because lab equipment often has a long lifetime, the impact of adding these appliances may be negligible in relation to the materials and energy inputs if the equipment is used to produce a large quantity of MgO particles. Other areas that this study did not explore are the energy costs of transporting material, or the effects of scaling

production. The estimations made for the energy consumption of the oven and furnace may be very high as no empirical data was collected.

5. Conclusions

MgO particles produced by microwave synthesis form well-defined nanocubes with a wide distribution of sizes including microscale particles (16 to 350 nm). MgO nanoparticles produced by aqueous synthesis are rounder than those produced by microwave synthesis and appear to have a narrower size distribution (between 30 and 90 nm).

At laboratory scale, the embodied energy and GWP of MgO nanoparticles produced using the microwave synthesis method (5970 ± 550 MJ/kg and 416 ± 59 kg CO_2/kg, respectively) were found to be significantly less than those produced by aqueous synthesis ($749,209 \pm 28$ MJ/kg and 42579 ± 11 kg CO_2/kg, respectively) using LCA.

6. Acknowledgments

7. References

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