analytical chemistry

Article

Cite This: Anal. Chem. XXXX, XXX, XXX−XXX

pubs.acs.org/ac

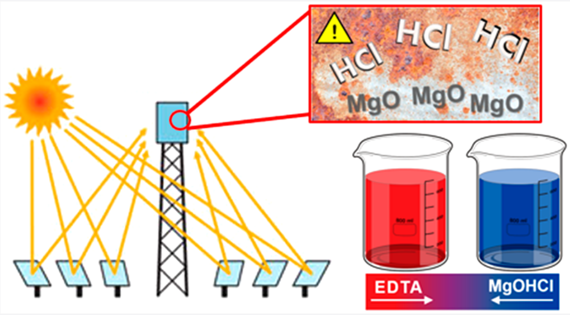
Method To Determine MgO and MgOHCl in Chloride Molten Salts

Noah Klammer, Chaiwat Engtrakul, Youyang Zhao, Yilin Wu, and Judith Vidal*

Thermal Sciences Group, National Renewable Energy Laboratory, Golden, Colorado 80401, United States

Supporting Information

ABSTRACT: A commercial blend of mainly carnallite ($KCl·MgCl_2·6H_2O$) is considered as a next-generation heat transfer fluid in solar thermal plants. Corrosive properties of $MgCl_2$ hydrates must be addressed at the operating temperatures of 500−720 °C. For successful chemical monitoring of the carnallite heat transfer fluid, an experimental method was developed to separate and titrate for MgO and MgOHCl from solid carnallite. This new method was assessed for error and accuracy. The method's relative error for MgOHCl was −7.0% for a mass fraction of 9.0 wt % MgOHCl in the carnallite salt. The method's relative error for MgO was less than +1.0% for a mass fraction of 12.0 wt % MgO in the carnallite salt. Titration results were used to track changes in the MgOHCl concentration in carnallite salt through the carnallite's dehydration and purification.



Next-generation concentrating solar power (CSP) technologies will benefit from the introduction of high-temperature, low-cost heat transfer fluids for dispatchable electricity generation with thermal energy storage. One avenue for continued cost reduction of CSP includes increasing the heat transfer fluid (HTF) operating temperature to the 500−700 °C regime. Current state-of-the-art nitrate salts are not stable in this regime, and so a new HTF is sought.[1]

For the next generation of CSP plants, many earth-abundant materials have been proposed and evaluated as HTFs.[1−6] The ternary chloride blend $NaCl/KCl/MgCl_2$ promises low material costs and desirable thermal properties.[7−11] However, the value of $MgCl_2$-containing HTFs is lost if $MgCl_2$ is hydrolyzed to MgOHCl during the heating and melting of the chloride blend. The unintended conversion of $MgCl_2$ to MgOHCl is a twofold problem. First, HTF composition is shifted because of the formation of MgOHCl. Second, the concentration of MgOHCl is correlated to the corrosion rate of internal tank surfaces because both the formation and thermal decomposition of MgOHCl form corrosive HCl gas.[12] The path to a viable $MgCl_2$-containing HTF relies on the successful dehydration of $MgCl_2$ hydrates and a robust measurement technique for MgOHCl and its thermal decomposition product MgO.

Limited literature exists on the physical and chemical properties of MgOHCl, which is formed in the heating of $MgCl_2$ hydrates but is not stable beyond 550 °C. It is known that, at temperatures greater than 350 °C, MgOHCl starts to thermally decompose to MgO and HCl.[12] As a result, it has been difficult to quantify MgOHCl in the salt. Though there have been few publications on the physical and chemical properties of MgOHCl, its accurate measurement is important for both the CSP and magnesium production industries. The consequences of MgOHCl formation in $MgCl_2$ hydrates is well-known in the magnesium industry, where it corrodes production equipment and reduces productivity.[12−14] Many of the takeaways from this work apply to both the CSP and magnesium industries.

The present work treats a commercial carnallite salt and sodium chloride ($KCl·MgCl_2·xH_2O$, NaCl). A possible molten salt production process is shown in Figure 1. Here, the hygroscopic carnallite is first dehydrated. The formation of MgOHCl occurs in the hydrolysis of $MgCl_2$ during dehydration.[12] To optimize the dehydration process and the resulting salt composition, we seek a MgOHCl and MgO measurement method that is simple and easily deployable in the life cycle of the molten salt (Figure 1). The effect of temperature on MgOHCl and MgO content in the carnallite salt was both a primary motivation and a proving ground for the method and is discussed below.

Existing methods for quantifying MgOHCl and MgO in the melt are not universally applicable. These methods typically did not report accuracy and standard deviation in their results and studied a specific use case only.[8,15−18] For example, Ding et al. recently tested an electrochemical sensor for MgOHCl and calibrated the sensor using a simple acid−base titration.[8] The titration results served as a primary standard for the electrochemical sensing. It was assumed that $MgOH^+$ was the predominant dissolved species in the salt melt and therefore the only acid-consuming compound. This assumption limits the method from sampling any MgO-containing regions in the salt which is not practical for commercial salts. Additionally, the presence of any dissolved metal and metal oxides in molten salt[19] cannot guarantee that $MgOH^+$ would be the only acid-

Received: September 20, 2019
Accepted: December 23, 2019

ACS Publications

DOI: 10.1021/acs.analchem.9b04301

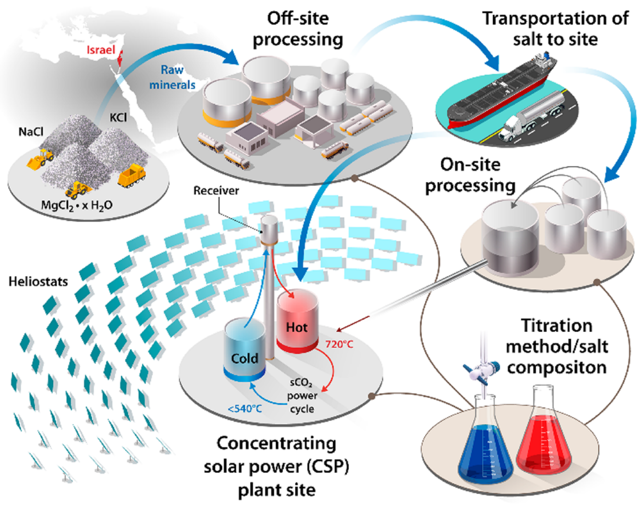


Figure 1. Context of the titration method in the proposed CSP plant operations. Earth-abundant chloride salts will be processed for use in the thermal energy storage of the plant. If $MgCl_2$ in the industrial blends is lost to MgOHCl, the proposed titration method can detect the compositional shift.

consuming compound. With this assumption, the measurement of MgOHCl by acid−base titration will not be accurate.

Kashani-Nejad et al. used X-ray diffraction (XRD) to support a speciation technique to measure MgO and $Mg_x(OH)_yCl_z$ relying on a difference of acid consumption—by acid−base titration—after calcination of MgOHCl.[16,18,20,21] This method required comparison between two separate powder samples. Lacking an analysis of experimental errors, the results were impractical to replicate.

Carbothermal reduction analysis was used by Mediaas et al. to distinguish MgO from MgOHCl.[22] However, in this analysis, moisture or any extra oxygen source would interfere with the measurement. Additionally, the carbothermal reduction required an additional reactor with toxic carbon monoxide as a reaction gas and infrared spectroscopy for a semiquantitative result. Such reliance on toxic gas and instrumentation impedes the deployment in the field.

Laroche et al. proposed that the difference in reaction kinetics between MgOHCl and HCl(aq) and that between MgO and HCl(aq) would allow for two rates of acid consumption.[17] Assuming an acid-attack model, back-calculating the acid consumption attained by acid−base titration would allow for determination of MgOHCl and MgO. However, samples with a low MgOHCl/MgO ratio proved exceptionally difficult to speciate. The authors stated that the method is semiquantitative and knowledge of oxide ratios and particle sizes is needed a priori.

Ultimately, the strengths and weaknesses of each method were considered to develop a more robust method. Here, an extraction procedure was developed to separate MgO from MgOHCl and remove NaCl, KCl, and $MgCl_2$ based on their different solubilities in a solvent (e.g., methanol and water). The separated MgO and MgOHCl were digested and titrated using a well-proven technique.[23−27] With blind trials by various users, we arrived at a method that is deemed to be user-friendly to a wide range of experience levels. Using the method described in detail in the Supporting Information, any user should be able to complete the method confidently and safely without complex instrumentation.

■ EXPERIMENTAL SECTION

Sample Preparation. The commercial carnallite was supplied by Israel Chemicals Ltd. (ICL) under the trade name QuicK-Mg. On the basis of multiple inductively coupled plasma atomic emission spectroscopy (ICP-AES) measurements, the salt was about 3/43/54 wt % NaCl/KCl/$MgCl_2$. The carnallite salt was stored in a glovebox where H_2O and O_2 concentrations were less than 0.5 ppm. To measure the accuracy of the titration, artificial salt standards were created at the above-mentioned composition. Reagent-grade chemicals, NaCl, KCl, and $MgCl_2$ (Alfa Aesar, >98% purity), were used in the artificial standards. The MgO was purchased from Martin Marietta (98%).

The MgOHCl is not available commercially but was synthesized from reagent $MgCl_2 \cdot 6H_2O$ (Sigma-Aldrich, BioUltra) using an existing method published elsewhere.[21] Briefly, the $MgCl_2 \cdot 6H_2O$ was heated in a tube furnace from room temperature to 376 °C at 5 °C/min under ambient air. The sample was then maintained at 376 °C for 30 min and cooled to room temperature without active furnace cooling. The crystal structure of the resulting product was examined with powder XRD (Figure 2) and matched reasonably well with the synthesized MgOHCl diffraction pattern reported by Kashani-Nejad et al.[21]

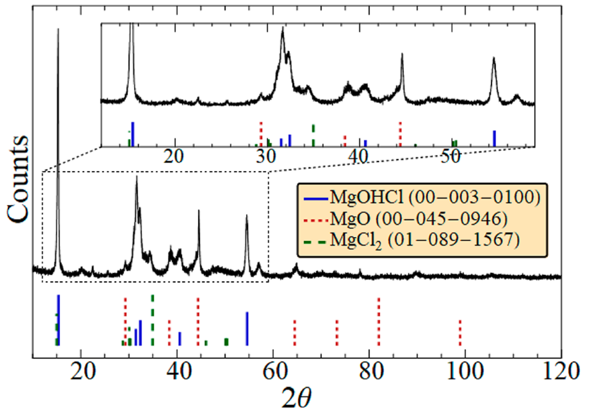


Figure 2. X-ray diffraction pattern of synthesized MgOHCl. The synthesized MgOHCl was examined using XRD and matches reasonably well to previously reported data (ref 21). Reference diffraction patterns and files are provided for MgOHCl (blue solid line), MgO (red dashed line), and $MgCl_2$ (green dashed line) (refs 30−32).

Kashani-Nejad et al., with an acid−base titration method, quantified their synthesized MgOHCl purity as 95%.[21] The purity of the synthesized MgOHCl in the present work was determined to be 80 ± 3 wt % using the same acid−base titration method described by Kashani-Nejad et al.[21] The purity of the synthesized MgOHCl is a result of the experimental conditions utilized to dehydrate $MgCl_2 \cdot 6H_2O$. Dehydrated $MgCl_2$ can only be converted to MgOHCl under certain conditions.[12,16] Although our MgOHCl was synthesized following a published method in order to avoid the formation of MgO, MgO formation has been reported at temperatures lower than the temperature utilized following this method.[28,29]

Supported by the XRD pattern in Figure 2 and the experimental conditions, the dominant species was MgOHCl, and the remaining 20% was likely a combination of MgO and

DOI: 10.1021/acs.analchem.9b04301
Anal. Chem. XXXX, XXX, XXX−XXX

$MgCl_2$.[12,16] Since XRD is not typically used to quantify mass or mole fraction of components present, we did not intend to quantify the relative amounts of $MgCl_2$ and MgO. To account for the purity of the synthesized MgOHCl (80%), a factor of 0.8 was applied to all pertinent calculations. The salt standard for testing MgOHCl detection was spiked with 12.3 wt % synthesized MgOHCl. The salt standard for testing MgO detection was spiked with 9.4 wt % MgO (98%, Martin Marietta).

The present work aims to purify and optimize commercially available carnallite salt for use in CSP application. Building on the salt dehydration process reported by others,[12,14] the carnallite salt was held at 117, 180, 240, 400, and 600 °C (the expected salt melting temperature is around 400 °C). MgOHCl is produced during $MgCl_2$ hydrolysis that occurs in parallel to the dehydration process. However, MgOHCl thermally decomposes by MgOHCl → MgO + HCl above 500−550 °C. Dwell time of each isotherm is expected to affect MgOHCl and MgO production accordingly in the carnallite salt.

The carnallite salt was heated in a custom-fabricated cylindrical test vessel with a quartz liner inside a vertical crucible furnace (ThermoScientific Blue M). The carnallite salt in powder form was poured into a nickel crucible with a lid (Daigger, SKU EF5641D) and heated to the said temperatures under a purge gas of 99.999% N_2 at 50 mL/min. After thermal purification, the purified carnallite was stored in the glovebox.

Instrumentation. Powder X-ray diffraction characterization of samples was done using a PANalytical PW3040 with an Empyrean Cu source. The working potential was 45 kV, and the working current was 40 mA. ICP-AES was performed on a PerkinElmer (PE) Optima 8300 with a PE Flatplate Optima 8x00 torch. The nebulizer gas was flowing at 680 mL/min, and the pump rate for the sample was 1.20 mL/min. Each ICP-AES sample was done in triplicate.

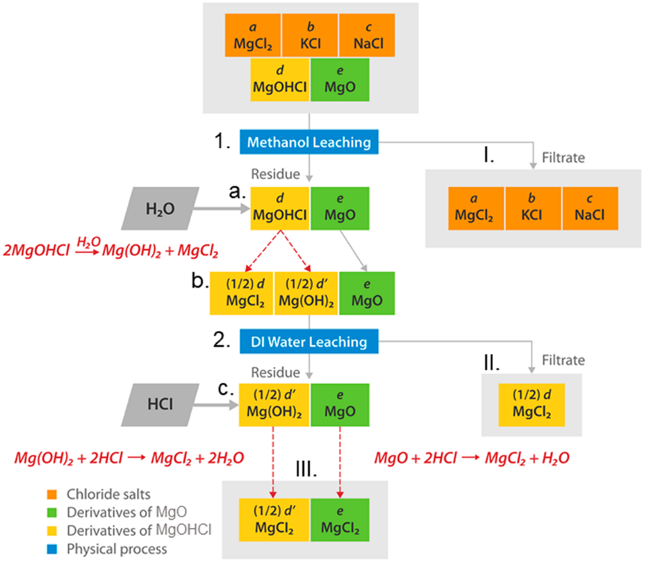
Extraction. The detailed method for extraction and titration of MgOHCl and MgO is provided in the Supporting Information. One assumption of this extraction method is that MgOHCl decomposes in water on a stoichiometric basis

$$MgOHCl \xrightarrow{\text{in water}} (1/2)Mg(OH)_2 + (1/2)MgCl_2 \qquad (1)$$

given by Savinkova et al.[33] However, experimental confirmation was difficult to find in the literature. Therefore, this assumption is assessed empirically in the Results and Discussion section.

Scheme 1 provides a process flow diagram for the method. A 500 mg sample of salt in powder form was immersed in 250 mL of methanol (Fisher Scientific, electronics grade) for 1 h to extract NaCl, KCl, and $MgCl_2$ based on the methanol solubilities of the major salt components at room temperature (Table 1). Additional details are given in the Supporting Information. As the solubilities of MgOHCl and MgO in methanol are 3 orders of magnitude less than those of the NaCl, KCl, and $MgCl_2$, it was assumed that the extracted masses of MgOHCl and MgO during methanol leaching were negligible. Likewise, the solubilities of MgO and $Mg(OH)_2$ in water were assumed to be negligible such that the extracted masses of MgO and $Mg(OH)_2$ during water leaching were negligible. Note that there is no process during titration where $Mg(OH)_2$ needs to be dissolved in methanol, and as indicated by eq 1, MgOHCl reacts to form $Mg(OH)_2$ in water. Therefore, we did not report solubility of $Mg(OH)_2$ in methanol and MgOHCl solubility in water because they are not relevant to the titration process.

Scheme 1. Separation and Titration Process Flow Diagram[a]



[a]Chemicals are colored to help keep track of the flow of each chemical. Gray arrows represent a physical process, and dashed red arrows represent a chemical process. The derivatives of MgOHCl and MgO are shown in yellow and green, respectively. Roman numerals (I, II, III) on the gray boxes represent a solution of one or more chemicals. Leaching steps are labeled with Arabic numerals (1, 2). Filter residues after the leaching steps are labeled with the Roman alphabet (a, b, c).

The methanol suspension of sample was filtered through a vacuum filter apparatus with a nylon filter membrane (GE Life Sciences cat. no. 7404-004, pore size 0.45 μm) (1). The resulting methanol filtrate (I) was either discarded or dried for future ICP analysis. The remaining filter residue and filter membrane (a) were transferred into a beaker of reagent deionized water. We assumed that water decomposes MgOHCl and dissolves $MgCl_2$ but not MgO or $Mg(OH)_2$—resulting from eq 1—based on the solubilities in water (Table 1). This suspension in water was agitated and filtered through a second filter membrane (2). The two consecutive extractions and filtrations resulted in two filtrates and one residue: methanol filtrate (I), water filtrate (II), and residue including both filter membranes (c). The latter residue was digested in HCl solution and appropriately buffered for titration (III). Note, the filter membranes were kept with the solution after the residue was digested.

In a typical ethylenediaminetetraacetic acid (EDTA) titration technique, EDTA (Sigma-Aldrich, ACS reagent grade, CAS 6381-92-6) complexes divalent metal ions, like Mg^{2+}, with a corresponding color change. The technique is borrowed from the American Public Health Association's Standard 2340: Hardness Determination in Water.[26] Our adaptation used a 0.0250 M EDTA titrant and a calmagite indicator solution (Sigma-Aldrich, indicator grade, CAS 3147-14-6). All procedural instructions are given in the hardness determination standard as well as in the Supporting Information. In the titration of the digested residue (III), cyclohexanediaminetetraacetic acid, disodium magnesium trihydrate salt—also known as magnesium salt of CDTA (CAS 63451-33-2, Hach Company, Inc.)—was used to obtain

DOI: 10.1021/acs.analchem.9b04301

Table 1. Solubilities of Selected Compounds in Methanol (CH_3OH) and Water (H_2O) at Room Temperature[a]

	NaCl (g/L)	KCl (g/L)	$MgCl_2$ (g/L)	MgO (g/L)	MgOHCl (g/L)	$Mg(OH)_2$ (g/L)
CH_3OH	14.9	3.95	11.3	0.0015	0.013	b
H_2O	360	344	546	0.086	b	0.009

[a] Refs 21 and 34. [b] Values not relevant to the described titration method.

a distinct end point in the presence of possible interference from other metal ions.[25,26,35]

Determination of MgOHCl and MgO. By leveraging the physical and chemical separations shown in Scheme 1, the determination of Mg^{2+} content can be used to calculate the MgOHCl and MgO present in the starting sample. Following the stoichiometries in Scheme 1, where the italicized letters represent the number of moles for each compound, Mg^{2+} in the water filtrate (II), i.e., from $MgCl_2$ derived from MgOHCl, is half the total Mg^{2+} in MgOHCl based on eq 1. The total moles of MgOHCl [d] can then be calculated as

$$d = 2n_{Mg^{2+},II} \tag{2}$$

where $n_{Mg^{2+},II}$ is the moles of Mg^{2+} in the water filtrate given by EDTA titration. The moles of MgO [e] in the residue filtrate (III) can be calculated from the moles of Mg^{2+} in the digested residue $n_{Mg^{2+},II}$ subtracted by the Mg^{2+} contribution from $MgCl_2$ [$(1/2)d'$]. The working assumption was that the reaction of MgOHCl in H_2O would produce $Mg(OH)_2$ and $MgCl_2$ in equal parts (eq 1), meaning that $(1/2)d' = (1/2)d$.[33] The moles of MgO [e] is then given by

$$e = n_{Mg^{2+},III} - n_{Mg^{2+},II} \tag{3}$$

RESULTS AND DISCUSSION

Mass Balance. Initial trials performed by the present authors to determine MgOHCl and MgO by the acid−base titration method of Ding et al.[36] and Kashani-Nejad[18] were unsatisfactory due to their analytical limits stated previously.

A central aim of this paper was to demonstrate the efficacy of the method presented so that other researchers may incorporate it into their own work. To that end, the separation process shown in Scheme 1 was examined, and ICP-AES was used to determine the Mg^{2+} in the initial salt, the methanol filtrate (I), the water filtrate (II), and the digested residue (III). The ICP-determined concentrations of Mg^{2+} were used to check the mass balance of the moles of Mg^{2+} in the water filtrate (I), methanol filtrate (II), and the digested residue (III) compared to those in the initial sample. Figure 3 shows the mass balance results for three salts with different levels of MgOHCl impurity: raw, thermally purified, and thermally and chemically purified. Details pertaining to the purification procedure for the raw salt are discussed elsewhere.[37]

As seen in Figure 3, the mass balance analysis for the extraction procedure produced more than 94% Mg^{2+} recovery for each of the three separate salt samples. Additionally, reasonable agreement between Mg^{2+} concentration measured by ICP-AES and titration was observed for these samples demonstrating the efficacy of the method.

Test with Artificial Salt Standards. To test the procedure's ability to distinguish between MgOHCl and MgO, we prepared artificial standards containing the representative amounts of MgOHCl and MgO typically observed in the carnallite salt. One set of standards contained 2.7/38.9/48.9 wt % NaCl/KCl/$MgCl_2$ and 9.4 wt % reagent MgO. The other set of standards contained 2.6/37.7/47.4 wt % NaCl/KCl/$MgCl_2$ and 12.3 wt % synthesized MgOHCl with $MgCl_2$ and MgO (see Figure 2). The titration results are shown in solid blue in Figure 4. The titration for both sets of standards was informative in that the average of three trials reproduced satisfactory accuracy and precision, as previously reported in the standard method for water hardness.[26]

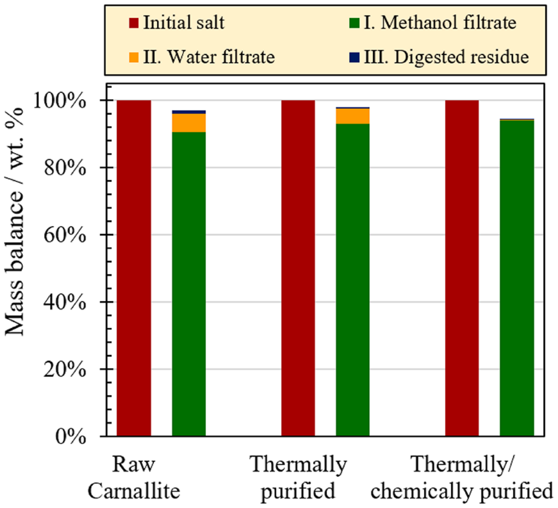


Figure 3. Mass balance of Mg^{2+} obtained with ICP-AES comparing the concentration in the initial salt (red) to the sum of concentrations after separation [methanol filtrate (I), water filtrate (II), and digested residue (III)]. The use of Roman numerals in the legend is consistent with that in Scheme 1.

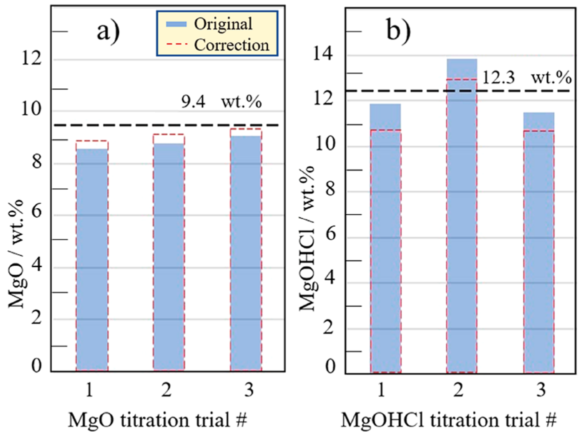


Figure 4. Results of titration (blue columns) for (a) MgO in 2.7/38.9/48.9/9.4 wt % NaCl/KCl/$MgCl_2$/MgO and (b) MgOHCl in 2.6/37.7/47.4/12.3 wt % NaCl/KCl/$MgCl_2$/MgOHCl. Corrected data by the water solubility of MgO and $Mg(OH)_2$ are shown as red dashed columns.

In testing carnallite salt after dehydration, many of our titration results gave negative false values for MgO mass fraction in cases where the real mass fraction of MgO was expected to be much less than the real mass fraction of

MgOHCl. Given the acceptable mass recovery via the mass balance shown in Figure 3, another mechanism had to be responsible for these false-detection values.

As a first approach, we set to eliminate the interference from other metal ions that might be affecting the complexation of the Mg−EDTA in the digested residue solution (III in Scheme 1) during titration. To remedy this interference, it is recommended to add magnesium salt of CDTA.[26] Even with this addition, the false values in the standards persisted.

An alternative hypothesis was that the solubility of MgO and $Mg(OH)_2$ in water (86 and 9 mg/L, respectively)[34] was not negligible in our analytical technique as we assumed. It was hypothesized that the soluble MgO and $Mg(OH)_2$ leave the filter's residue and enter the water filtrate thus adding to the total Mg^{2+} detected by titration. Using values from Table 1 and from Figure 4, one can calculate the minimum volume of water solvent needed to account for the false detections. This volume was always less than or equal to the volume of water used in the procedure. Therefore, the hypothesis that the false detections were due to nonzero solubilities of MgO and $Mg(OH)_2$ is supported.

Another plausible hypothesis for the negative values for MgO was that the MgO by titration (eq 3) was subject to indistinct color change of the indicator at the titration end points in the digested residue (III). Indistinct end points in the digested residue (III) for small MgO mass fraction might give errors in $n_{Mg2+,III}$ of comparable magnitude to the difference of $n_{Mg2+,III}$ and $n_{Mg2+,II}$, a problem from the standpoint of error propagation. Additionally, a known weakness of earlier iterations of the procedure was the slow kinetics of MgO dissolution with HCl(aq).[30]

To investigate potential errors in the low mass fraction MgO regime, a series of masses of MgO (5.0, 0.5, and 0.2 mg, representing 1.00, 0.10, and 0.04 wt %, respectively) were digested, and then titrated. At each MgO mass, MgO measured by titration in five replicates is nearly equal to reagent MgO added. Even at the 0.2 mg MgO (i.e., 0.04 wt % MgO), the average accuracy and relative standard deviation for the five trials were 87% and 18%, respectively. With this accuracy for MgO concentration by titration at low mass fraction of MgO, the error propagation from $n_{Mg2+,III}$ by titration was unlikely to be responsible for the negative MgO values.

Therefore, if small concentrations of MgO and $Mg(OH)_2$ were dissolved and passed from the residue (c in Scheme 1) into the water filtrate (II) during the water leaching step (2), the water filtrate (II) would have extra moles of Mg^{2+} and the digested residue (III) would lack the said moles of Mg^{2+}. A logical next step would be to apply this theory to the moles of Mg^{2+} by titration in both the water filtrate (II), $n_{Mg2+,II}$, and in the digested residue (III), $n_{Mg2+,III}$. In Figure 4, the MgO and $Mg(OH)_2$ concentrations corrected by their solubilities in water are shown in red dashed columns.

In the case of the standard with no MgOHCl (Figure 4a), the number of moles of Mg^{2+} in the water filtrate (II), $n_{Mg2+,II}$, was greater than the expected value of zero. $n_{Mg2+,II}$ should be equal to zero as there was no MgOHCl present in that artificial standard (see eq 2). To correct for this, a solubility correction factor of $\delta_{Mg2+,II}$ was subtracted from the moles of MgOHCl $[n_{Mg2+,II}]$ and added onto the moles of MgO $[e]$:

$$d' = 0 = 2(n_{Mg^{2+},II} - \delta_{Mg^{2+},II}) \tag{4}$$

$$e' = (n_{Mg^{2+},III} - n_{Mg^{2+},II}) + \delta_{Mg^{2+},II} \tag{5}$$

The correction, seen in dashed red columns in Figure 4a, brings the average MgO accuracy of the three titrations from 93% to 96%. The counterpart of this correction to eq 3 was made for the artificial standard with no MgO in a similar manner (Figure 4b). However, this correction brings the average MgOHCl accuracy of the titrations from 101% to 93%. The corrections by MgO and $Mg(OH)_2$ solubilities in water as shown Figure 4 seem to confirm our hypothesis that MgO and $Mg(OH)_2$ cannot be taken to be virtually insoluble in this application. We recommend that users perform their own analysis with their titration results to determine if the correction for limited solubility of MgO and $Mg(OH)_2$ is necessary.

Practical Detection Limit. The next experiment we pursued was to see to what degree the presence of MgOHCl or MgO would interfere with the determination of the other. A secondary goal of the experiment was to determine if the mass fraction range of MgOHCl or MgO that resulted in negative MgO concentration values could be identified. Figure 5 shows the results for a dehydrated carnallite salt with added reagent MgO. By increasing the concentration of MgO artificially, we expected to see a corresponding response in the determination of MgOHCl and MgO. The theoretical MgO wt % was expected to increase as reagent MgO was added (shown as the blue dashed line intersecting the origin), while the theoretical MgOHCl wt % would decrease.

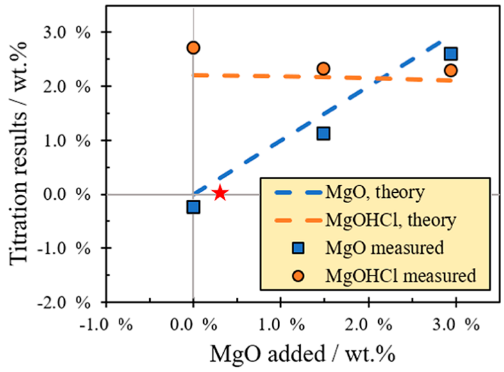


Figure 5. Titration results (blue squares and orange circles) and theoretical calculation (blue and orange dashed lines) of MgO and MgOHCl in a dehydrated carnallite salt as a function of MgO reagent added. The red star represents the *x*-axis intercept of the best-fit line for measured MgO at 0.3 wt % and likely the lowest weight percent of MgO where a nonzero determination is possible.

Experimental measurements of MgO (blue squares) show linear behavior ($R^2 = 0.999$) in this compositional regime with an intercept of *x*-axis at 0.3 wt % (red star in Figure 5). This intercept implies that the minimum concentration of MgO to give non-negative method results is about 0.3 wt % MgO. The minimum quantification limit for this method has not been comprehensively determined but is above the 0.3 wt % MgO mass fraction. Lower minimum quantification limits may be possible by adjusting sample size, filter pore size, EDTA titrant molarity, etc., from those given in the Supporting Information. Figure 5 proves that the negative values of MgO previously discussed are not an insurmountable flaw in the method.

Our working assumption that MgOHCl dissociates stoichiometrically into equal parts $Mg(OH)_2$ and $MgCl_2$ in water was held as plausible through the results of Figures 4 and 5. If the decomposition of MgOHCl in water could not be accurately

DOI: 10.1021/acs.analchem.9b04301
Anal. Chem. XXXX, XXX, XXX−XXX

described by eq 1, then the results in Figures 4 and 5 would show greater variation and/or reduced accuracy. Although stoichiometries of $Mg_x(OH)_yCl_z$ other than x, y, z = 1 are known,[38,39] our results indicate that MgOHCl is the predominant stoichiometry and that other magnesium hydroxychloride compounds can be neglected.

Finally, a practical application of the titration method is presented in Figure 6 which shows the MgOHCl mass fraction in the carnallite salt at different stages of purification. The mass fraction of MgOHCl is around 0.3 wt % in the chemically purified carnallite. The method helps to optimize the process of salt dehydration and purification by measuring the formation of MgOHCl. After the completion of each dehydration step, a solidified sample of salt is taken for titration. The increase of MgOHCl mass fraction during the 117, 240, and 400 °C steps is consistent with the literature as is its decrease at 600 °C.[12] When metallic magnesium was added as a reducing agent to the MgOHCl (chemical purification column in Figure 6) the mass fraction of MgOHCl decreased, consistent with the literature.[8] The method has been evaluated for accuracy and consistency with MgOHCl concentration in the range of 0.3−9.0 wt % as shown in Figure 6 with the commercial carnallite supplied by ICL. On the basis of recent efforts,[35] where a higher purity commercial carnallite and an improved salt purification process were used, 0.11 ± 0.02 wt % of MgOHCl was measured (based on more than 10 samples) using a more diluted EDTA solution (i.e., 5× more diluted than the original 0.0250 M given in the Experimental Section). Therefore, based on our experimental results, a level of MgOHCl can be confidently measured down to ∼0.1 wt %. Investigation of the detection limit at lower MgOHCl concentration (e.g., 10−100 ppm) has not been performed due to the lack of commercially available salts with low levels of MgOHCl and a salt purification process that can achieve these low levels of MgOHCl. We believe that using an artificial salt mixture with the synthesized MgOHCl is not adequate due to the current purity of the synthesized MgOHCl (i.e., ∼80%). In addition, we acknowledge that only reagent grade salts of >98% purity were tested in the present work because the described titration method was developed with the mindset that end users, including not only advanced analytical chemistry laboratories but also remote concentrating solar power plants and/or salt-processing plants, can use this method. The accuracy of the titration method can be further improved by using higher purity chemicals, if available.

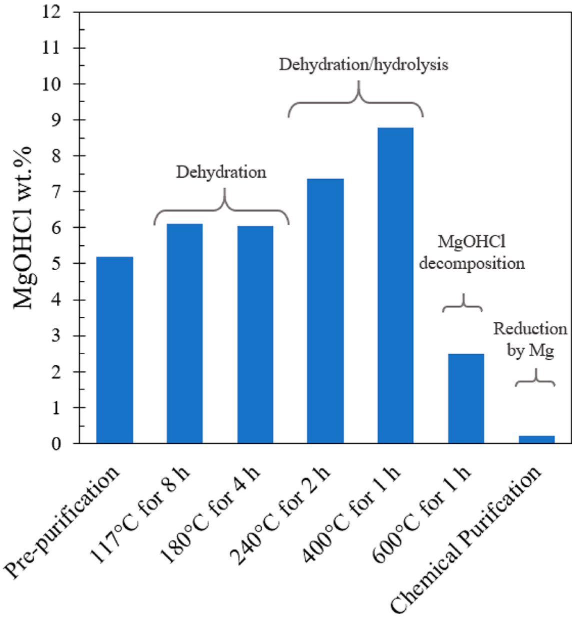


Figure 6. MgOHCl (by titration) in carnallite salt at each dehydration isotherm. The method is used to inform our knowledge of the chemical reactions during dehydration of the salt. The concentration of MgOHCl is seen to rise at the 117, 180, 240, and 400 °C dehydration stages. MgOHCl falls at the 600 °C segment due to thermal decomposition at ∼550 °C. Finally, remaining MgOHCl can be further decreased by reduction by metallic Mg.

Impact. The CSP and magnesium metal industries will benefit from a method to determine MgOHCl and MgO since both species will lower the production efficiency of the magnesium electrolysis process. The presented method is extremely low cost compared to other analytical chemistry instrumentation and can be performed with basic laboratory equipment. Although interference from other divalent ions can be present, many feedstocks for magnesium electrolysis (e.g., magnesite, dolomite, bischofite, carnallite, serpentine) contain low concentrations of these divalent ions.[40]

■ CONCLUSIONS

We have demonstrated and validated an easily deployable, robust method for determining MgOHCl and MgO in $MgCl_2$-containing chloride salts. An extraction of solutions using methanol and then water followed by a common EDTA titration procedure shows significant improvement over previously reported methods. Our results also show that the method is reasonable in mass fraction regimes as low as 1.0 wt % MgO and 0.3 wt % MgOHCl and can be further improved to a few hundred parts per million by modifying the concentration of the EDTA solution. The method was verified by users with varying levels of chemical expertise.

Accurate measurement of MgOHCl and MgO underpins ongoing and future work in optimizing chemistries in $MgCl_2$-containing chloride salts. The method makes possible the calibration of future development of other MgOHCl sensing techniques, e.g., in situ and continuous electrochemical sensors for industrial applications.[36,41]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.analchem.9b04301.

Procedural method for the determination of MgO and MgOHCl in chloride salts by titration (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: Judith.Vidal@nrel.gov.

ORCID

Noah Klammer: 0000-0001-8181-3182
Chaiwat Engtrakul: 0000-0002-8773-0668
Yilin Wu: 0000-0002-8331-3744

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was authored by the Alliance for Sustainable Energy, LLC, the manager and operator of the National Renewable Energy Laboratory for the U.S. Department of Energy (DOE) under contract no. DE-EE00033870. Funding was provided by the U.S. Department of Energy Office of Science, Office of Workforce Development for Teachers and Scientists (WDTS) under the Community College Internship (CCI) program and the Science Undergraduate Laboratory Internship (SULI) program, and the Office of Energy Efficiency and Renewable Energy, Solar Energy Technologies office. The views expressed in the article do not necessarily represent the views of the DOE or the U.S. Government. The U.S. Government retains and the publisher, by accepting the article for publication, acknowledges that the U.S. Government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for U.S. Government purposes. The authors gratefully acknowledge Jakob Chandler and Zack Krajnak for their contributions.

REFERENCES

(1) Mehos, M.; Turchi, C.; Vidal, J.; Wagner, M.; Ma, Z.; Ho, C.; Kolb, W.; Andraka, C.; Kruizenga, A. *Concentrating Solar Power Gen3 Demonstration Roadmap*; NREL/TP-5500-67464; U.S. Department of Energy Office of Scientific and Technical Information: United States, 2017. .

(2) Gomez, J. C.; Calvet, N.; Starace, A. K.; Glatzmaier, G. C. *J. Sol. Energy Eng.* **2013**, *135* (2), 021016.

(3) Tian, Y.; Zhao, C. Y. *Appl. Energy* **2013**, *104*, 538−553.

(4) Gil, A.; Medrano, M.; Martorell, I.; Lazaro, A.; Dolado, P.; Zalba, B.; Cabeza, L. F. *Renewable Sustainable Energy Rev.* **2010**, *14*, 31−55.

(5) Li, Y.; Xu, X.; Wang, X.; Li, P.; Hao, Q.; Xiao, B. *Sol. Energy* **2017**, *152*, 57−79.

(6) Wei, X.; Song, M.; Wang, W.; Ding, J.; Yang, J. *Appl. Energy* **2015**, *156*, 306−310.

(7) Mohan, G.; Venkataraman, M.; Gomez-Vidal, J.; Coventry, J. *Energy Convers. Manage.* **2018**, *167* (April), 156−164.

(8) Ding, W.; Bonk, A.; Gussone, J.; Bauer, T. *J. Energy Storage* **2018**, *15*, 408−414.

(9) Ding, W.; Shi, H.; Jianu, A.; Xiu, Y.; Bonk, A.; Weisenburger, A.; Bauer, T. *Sol. Energy Mater. Sol. Cells* **2019**, *193*, 298−313.

(10) Ding, W.; Shi, H.; Xiu, Y.; Bonk, A.; Weisenburger, A.; Jianu, A.; Bauer, T. *Sol. Energy Mater. Sol. Cells* **2018**, *184* (April), 22−30.

(11) Ding, W.; Bonk, A.; Bauer, T. *Front. Chem. Sci. Eng.* **2018**, *12* (3), 564−576.

(12) Kipouros, G. J.; Sadoway, D. R. *J. Light Met.* **2001**, *1*, 111−117.

(13) Dead Sea Magnesium Ltd. Personal communication, 2018.

(14) Smith, A.; Veazey, W. Dehydration of Magnesium Chloride. U.S. Patent US1835818, 1929.

(15) Vindstad, J. E.; Mediaas, H.; Ostvold, T. *Acta Chem. Scand.* **1997**, *51*, 1192−1200.

(16) Kashani-Nejad, S.; Ng, K.-W.; Harris, R. *Metall. Mater. Trans. B* **2005**, *36* (1), 153−157.

(17) Laroche, D.; Davis, B. R.; Watson, K.; Ficara, P. Oxide Speciation in Magnesium Chloride Based Fused Salts. *Proceedings of the International Symposium on Light Metals*; Bouchard, M., Faucher, A., Eds.; Canadian Institute of Mining, Metallurgy and Petroleum: Montreal, Canada, 1999; pp 103−109.

(18) Kashani-Nejad, S. Oxides in the Dehydration of Magnesium Chloride Hexahydrate. *Ph.D. Thesis*, McGill University, 2005.

(19) Boghosian, S.; Godo, A.; Mediaas, H.; Ravlo, W.; Ostvold, T. *Acta Chem. Scand.* **1991**, *45*, 145−147.

(20) Kashani-Nejad, S.; Ng, K. W.; Harris, R. *Metall. Mater. Trans. B* **2004**, *35* (26), 406−408.

(21) Kashani-Nejad, S.; Ng, K. W.; Harris, R. *Metall. Mater. Trans. B* **2004**, *35* (4), 405−406.

(22) Mediaas, H.; Vindstad, J. E.; Ostvold, T. Solubility of MgO in $MgCl_2$−NaCl−NaF Melts. In *TMS Light Metals 1996*; Hale, W., Ed.; TMS: Warrendale, PA, 1996; pp 1129−1137.

(23) Betz, J. D.; Noll, C. A. *J. - Am. Water Works Assoc.* **1950**, *42* (1), 49−56.

(24) Diehl, H.; Goetz, C. A.; Hach, C. C. *J. - Am. Water Works Assoc.* **1950**, *42* (1), 40−48.

(25) Lindstrom, F.; Diehl, H. *Anal. Chem.* **1960**, *32* (9), 1123−1127.

(26) American Public Health Association. 2340: Hardness. In *Standard Methods for the Examination of Water and Wastewater*; Washington, DC, 1998; pp 37−39.

(27) Harris, D. C. EDTA Titrations. *Quantitative Chemical Analysis*; Freeman & Co.: New York, 2006.

(28) Huang, Q.; Lu, G.; Wang, J.; Yu, J. *J. Anal. Appl. Pyrolysis* **2011**, *91* (1), 159−164.

(29) de Bakker, J.; Peacey, J.; Davis, B. *Can. Metall. Q.* **2012**, *51* (4), 419−423.

(30) Feitknecht, W.; Held, F. *Helv. Chim. Acta* **1944**, *27*, 1480.

(31) Kabekkodu, S., Ed. *PDF-2*; ICCD: Newtown Square, PA, 2008.

(32) Partin, D. E.; O'Keeffe, M. *J. Solid State Chem.* **1991**, *95* (1), 176−183.

(33) Savinkova, E. I.; Lelekova, R. P.; Ibroyalovskaya, V.; Nikitina, S. A. Determination of Carnallite (MgO, MgOHCl) Hydrolysis Products by Alkalimetric Titration. Deposited Vitini. *Ural. Politekh. Inst. Sverdlovsk, USSR*, **1976**, 1127−1176.

(34) Patnaik, P. *Handbook of Inorganic Chemicals*; McGraw-Hill: New York, 2003.

(35) Smith, R. M.; Martell, A. E. Iminodiacetic Acid Derivatives. In *Critical Stability Constants*; Smith, R. M., Martell, A. E., Eds.; Springer: Boston, MA, 1989.

(36) Ding, W.; Bonk, A.; Gussone, J.; Bauer, T. *Energy Procedia* **2017**, *135*, 82−91.

(37) Zhao, Y.; Klammer, N.; Vidal, J. C. *RSC Adv.* **2019**, *9*, 41664−41671.

(38) Herbstein, F. H.; Kapon, M.; Weissman, A. *Isr. J. Chem.* **1982**, *22*, 207−213.

(39) Bodine, M. W. *Geology* **1976**, *4* (2), 76−80.

(40) Aghion, E.; Golub, G. Production Technologies of Magnesium. In *Technology of Magnesium and Magnesium Alloys*; Friedrich, H. E., Mordike, B., Eds.; Springer: Berlin Heidelberg, 2006; pp 29−62.

(41) Ding, W.; Vidal, J. C. In-Situ Electrochemical Sensor of Molten Chlorides. Patent application, 2019.

DOI: 10.1021/acs.analchem.9b04301