Modelling of the Erosive Dissolution of Metal Oxides in a Deep Eutectic Solvent—Choline Chloride/Sulfosalicylic Acid—Assisted by Ultrasonic Cavitation

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Abstract: Here we report on the results concerning the influence of ultrasound on the dissolution process of metal oxides CoO, Ni$_2$O$_3$ and Mn$_2$O$_3$ in choline chloride/sulfosalicylic acid as a deep eutectic solvent. The mechanism of dissolution under cavitation conditions with ultrasonic assistance is described. Theoretical research resulted in equations describing the dissolution process kinetics and linking its basic parameters. Optimal conditions for the most effective ultrasound application were found. Experimental data on dissolution kinetics of metal oxides in deep eutectic solvents was also obtained. It was discovered that experimental data correlates well with theoretical calculations, which confirms the correctness of developing a picture about the physicochemical nature of the process under study.

Keywords: ultrasonic cavitation; dissolution; deep eutectic solvent; metal oxides; Li-ion battery

1. Introduction

The dissolution (or leaching) process of one or several components in an appropriate solvent is widely applied in technological production [1–3]. One of the most efficient methods for the intensification of dissolution (leaching) of solid materials implies the use of ultrasound (US), which significantly reduces the process time and increases the product yield [4–8]. Earlier works have studied the effect of ultrasound on the extraction of organic and inorganic substances [9–14]. It is known that ultrasonic action allows one to improve the leaching process with traditional reagents [15–17]. Marafi et al., in their study devoted to the optimization of V, Mo, Ni extraction from acidic leaching solutions of spent catalysts, demonstrated that ultrasonic-induced stirring of an extraction system increases the rate of extraction and the proportion (>95%) of all extractable components [18]. According to recent research by Kong et al., which deals with leaching of iron from waste accumulating during production of photovoltaic modules, ultrasound is able to greatly intensify the extraction process (reduction of process time by 37.5%) by crushing the solid fraction into smaller ones, which in turn allows increasing the collision frequency of hydrogen ions with atoms of iron in solution [19]. The mechanism of US action consists of cavitational destruction of solids and surface films, stirring of liquid under the influence of acoustic flows and accelerated penetration of liquid into the pores and cracks of a solid. Pulsating cavitation bubbles induce micro flows near the phase boundary and provide removal of the reaction products and delivery of new portions of the reagent. In case the strength of solid surface is great enough for its particle’s separation under the influence of a pressure drop caused by the collapsing bubble but does not exceed the cracking threshold, the solution penetrates through capillaries deep into particles due to an acoustocapillary effect and promotes its dissolution. These and other features of US can efficiently show themselves and noticeably improve the performance of an US-leaching system only with strict adherence to all necessary parameters, which are determined from detailed physicochemical analysis of...
processes under consideration, taking into account the individual features of each scheme of realization of given technology. At the same time, the successful and useful adaptation for leaching purposes is possible and expedient for almost every nonlinear acoustic effect including cavitation, acoustic flow, nonlinear wave interaction, solitary impulses, etc. In this paper, on the basis of well-established ideas about the physical nature of ultrasonic cavitation erosion, original working formulas were obtained for the first time, which make it possible to quantify the parameters of the process of dissolving metals using ultrasound.

Due to intensive industrialization and high demand for electronic devices, the issue of their subsequent utilization is of great importance all over the world [20–23]. Besides the toxic heavy metals (Pb, Cd, Hg, As, etc.) that can leak into wastewater and soil as a result of inappropriate utilization, electronic waste contains a great many strategically important and valuable elements that can be reused after recovery [24,25]. Today, deep eutectic solvents (DES) are actively used for dissolution of metal oxides and salts contained in ore, chemical current sources, catalysts, etc. [26–28]. Abbot et al. were the first to use DES based on choline chloride for dissolution of metal oxides [29]. This study gave a start to development of hydrophilic DES and their application in metal extraction. As it was shown, DES based on choline chloride and carboxylic acids possess high dissolving ability [30].

The research on intensification of extraction of biologically active compounds from plant raw materials in DES-containing systems is presented by several works [31–33]. However, no literature concerning the ultrasonic-assisted intensification of metal oxides dissolution was found. Thus, the influence of US on kinetics of dissolution of target components should be understood to establish suitable working conditions for a dissolution rate increase. Since metals in solid components of used batteries, accumulators (Li-ion, Ni-MH) and other devices are often contained in the oxide forms of various oxidation states [34], CoO, Ni$_2$O$_3$, and Mn$_2$O$_3$ were used as model objects. The metals included in these oxides are valuable and widely used in the steel industry for stainless steel and special alloys production. It is also possible to reuse them for the aforementioned electrochemical devices production.

Previously we have studied the dissolving ability of DES based on choline chloride/sulfosalicylic acid with respect to nonferrous and rare-earth metals [35]. It was found that maximum solubility of their oxides in DES is achieved only after a long processing time (about 120 min). The purpose of the present research is to evaluate the possibility of CoO, Ni$_2$O$_3$, and Mn$_2$O$_3$ dissolution process intensification with the assistance of US in a DES environment. It should be noted that ultrasound affects the dissolution of metal oxides in DES, including the kinetics of the process. To achieve better understanding of the influence of cavitation erosion on dissolution parameters, it is important to study the case where other processes are not strongly affected by US. The correctness of the theoretical model can be demonstrated by the appropriate experiment design. When the other dissolution promoting processes are accelerated by US there is a possibility of a mismatch between the observations and the proposed mechanism. In this case, we only observed the combined effect, which includes the influence of the aspect under study.

2. Materials and Methods

2.1. Chemicals

Choline chloride (Acros Organics, 99%) and sulfosalicylic acid (chemically pure grade) were used without additional purification as an HBA and HBD, respectively. Cobalt(II) oxide, manganese(III) oxide, and nickel(III) oxide were used with a purity of >99%.

2.2. Experimental, Apparatus and Procedures

DES based on choline chloride/sulfosalicylic acid in molar ratio of 7:3 was used as a solvent. Reagents were weighed on analytical scalesHR-100AZ (AND, Tokyo, Japan) and then placed in 10 mL glass vials. For DES formation vials were stirred for 120 min (1250 rpm) at 90 °C on a magnetic stirrer C-MAG HS 4 (IKA, Staufen, Germany) in glycerin bath. The
investigation of Co(II), Ni(III) and Mn(III) oxides dissolution in DES was carried out in glass vials with a constant interphase area of 1.54 cm$^2$ at mass ratio of solid/liquid equal to 1:50. Experiments were performed in thermostatic conditions at 80 °C and stirring rate of 125 rpm. The ultrasonic generator Grad-Technology 28–35 C (Grad-Technology, Moscow, Russia) with a capacity of 110 W and a frequency of 35 kHz was used for experiments with ultrasound. The experimental setup is shown in Figure 1.

Figure 1. Experimental setup.

Metal concentration in DES after the oxide dissolution was determined spectrophotometrically after the pretreatment with 4-(2-pyridylazo)-resorcinol with formation of complexes absorbing in a visible spectrum at the following wavelengths (nm): Ni (495), Mn (499), Co (510) [36]. Optical densities were measured on Cary-60 (Agilent Tech, Santa Clara, California, United States) device in glass cuvettes with an optical path length of 10 mm. The concentration determination error was <5%.

All the experimental results were reproduced three times and processed via mathematical statistics methods.

3. Theoretical Part
3.1. Applicable Methods and Some Basic Schemes for Solving the Problem

Dissolution of solids promoted by ultrasound can be implemented operating with the latter as with a running (Figure 2a) or a standing wave (Figure 2b) or as a combination of waves at different frequencies. To achieve the maximum work efficiency in each case, it is highly important to keep the proportions of nodes location and the operation regimes to realize the capabilities of every nonlinear mechanism involved in the process. Figure 2a illustrates one of the simplest ways of interaction of metal oxide particle with ultrasonic running wave. In this case it is easy to change the affection point and the distance between the radiation source and the target, but it is difficult enough to precisely maintain the
necessary distance. For processing of flat surfaces in the case of plates, tapes or nets standing wave can be used according to Figure 2b.

**Figure 2.** Possible schemes of erosive action on solid particles with ultrasonic cavitation assistance: 1—ultrasonic emitter; 2—ultrasonic wave; 3—target; (a)—running ultrasonic wave usage; (b)—standing ultrasonic wave usage.

Such setup allows providing complete dissolution of metal oxide. Combined irradiation can be obtained by entering (to the Figure 2a or Figure 2b) of additional emitters working at a different frequency in the optimal positions, approved by corresponding calculations. Specification of each ultrasonic leaching scheme requires consideration of every used nonlinear acoustic mechanism contribution and performance of necessary calculations on this basis.

### 3.2. Force Component of the Ultrasonic Cavitation Action

Application of cavitation erosive properties for metal oxides dissolution in DES is based on the ability of cavitation bubbles to collapse and generate force waves, which in turn cause the destruction of barriers met on their way. Knowledge of basic patterns of such phenomena is useful for erosion rate calculation and determination of optimal bubbles size and the distance between the bunch they form and the target. The most suitable irradiation parameters’ ratio can also be obtained.

A step-by-step analysis of the force qualities of cavitation to obtain fairly simple final expressions can be performed using the equation Noltingk–Neppiras [37] wrote for the radius $R(t)$ of the cavitation bubble, the value of which varies in time $t$ according to the following known law. It is assumed that in the initial state bubble was in equilibrium with environment possessing the radius equal to $R_0$ and pressure $P_{10}$. $\rho_1(t)$—gas density inside the bubble, $\rho_2(t)$—density of external liquid.

$$R \frac{d^2 R}{dt^2} + \frac{3}{2} \left( \frac{dR}{dt} \right)^2 + \frac{1}{\rho_2} \left[ P_0 + \rho_m \sin \omega t + \frac{2\alpha}{R(t)} \right] - \left( P_0 + \frac{2\alpha}{R_0} - P_g \right) \left( \frac{R_0}{R(t)} \right)^3 - P_g = 0 \quad (1)$$

It should be noted that the Herring–Flynn equation [37], which generalizes Equation (1) in the case of viscosity and compressibility, more accurately describes the behavior of the cavitation bubble. But this correction is not critically important, and the cumbersomeness of the relations with which it is necessary to operate at the same time does not allow obtaining observable finite formulas. Therefore, as a first step in this consideration, it is possible to use Equation (1) as the initial equation, bearing in mind the always existing possibility of its generalization and refinement if necessary. Then from Equation (1) at any moment it turns out:

$$P_1(t) = P_{10} \left( \frac{R_0}{R(t)} \right)^3 + P_g = \left( P_0 + \frac{2\alpha}{R_0} - P_g \right) \left( \frac{R_0}{R(t)} \right)^3 + P_g \quad (2)$$
where $\gamma$—polytropic index, defined for gases through the equation $\gamma = c_p / c_v$ ($c_p$, $c_v$—heat capacities), $\alpha$—coefficient of surface tension, $2\alpha / R(t)$—the pressure caused by it, $P_0$—hydrostatic pressure of surrounding liquid in the initial state, $P_g$—steam pressure inside the bubble. Equilibrium of pressures on the bubble’s border leads to the following expression for the pressure on the border of the bubble $P(R)$:

$$P(R) = \left( P_0 + \frac{2\alpha}{R_0} - P_g \right) \left( \frac{R_0}{R(t)} \right)^{3\gamma} + P_g - \frac{2\alpha}{R(t)}$$

(3)

Pressure of liquid on the distance near the infinity $P(R \to \infty) = P_\infty$ in case of providing of ultrasonic action equal to $P_m \sin \omega t$ with pressure amplitude $P_m$ and frequency $\omega$ in equilibrium state can be presented as:

$$P_\infty = P_0 + P_m \sin \omega t$$

(4)

It is possible to apply Equation (1) when solving problems of nonlinear behavior of spherical surface of gas bubble in dynamics in case of simple pulsations as well as of complicated deformations under ultrasonic conditions.

Thus, the solution of Equation (1) gives an opportunity to determine the minimal radius of cavitation bubble during its collapse. In turn maximal surface pressure $P_{max}$ can be calculated using Equation (3). Integration of Equation (1) is simplified due to the reason that almost in all practically important cases the time of collapse is significantly lower than a quarter of ultrasound oscillation period $T = 2\pi / \omega$ so $P_m$ can be used instead of $P_m \sin \omega t$. As a result, the first integral of Equation (1) looks like:

$$\frac{3\alpha}{2} \left( \frac{dR}{dt} \right)^2 = P_c \left[ \left( \frac{R_{\max}}{R(t)} \right)^3 - 1 \right] + 3\alpha / R(t) \left[ \left( \frac{R_{\max}}{R(t)} \right)^2 - 1 \right] + P_S \left[ \left( \frac{R_{\max}}{R(t)} \right)^3 - \left( \frac{R_{\max}}{R(t)} \right)^{3\gamma} \right]$$

(5)

here $P_{00} = P_0 + 2\alpha / R_0 - P_g$, $P_c = P_0 + P_m - P_g$, $P_S = P_0 \frac{R_0}{\gamma - 1} \left( \frac{R_0}{R_{\max}} \right)^{3\gamma}$, and the extremum of function $R(t)$ reaching its maximum value $R_{\max}$ was used to derive Equation (5). The same extremus exists at the time of collapse when the radius of the bubble has a minimum value of $R_{\min}$. This makes it possible to define the $R_{\max} / R_{\min}$ ratio from Equation (2). Substituting this ratio in (1), it is possible to obtain an expression for the maximum pressure on the surface of the bubble $P_{max}$, since it is achieved at $R = R_{\min}$. The force exerted by this pressure of the shock wave coming from the collapsing bubble is capable of tearing a piece of metal oxide from the solid surface if the pressure $P_{max}$ exceeds the force determined by the yield strength $\sigma_t$ of the metal oxide, calculated per surface unit of the solid.

In most real conditions Equations (1) and (5) allow significant simplifications connected with practically used values of task parameters. As a result, it is possible to operate with compact expressions, allowing efficient examination of actual laws of solid surfaces cleaning from petroleum products. Therefore, in conditions when $P_c \gg 3\alpha / R_{\max}$ the term containing surface tension coefficient in Equation (6) can be missed. In most cases consideration of steam pressure is also irrelevant. Then for equilibrium condition of liquid with pressure $P_c = P_0 + P_m$ one can obtain the following expression for $R_{\max}$ through its equilibrium value $R_0$ (adiabatic bubble collapse, $\gamma = 4/3$):

$$R_{\max} \approx R_0 \left( \frac{P_c + P_0}{P_c} \right)^{1/3}$$

(6)

In the same way from Equation (5) formula for $R_{\min}$ in this case is derived:

$$R_{\min} \approx R_0 \left( \frac{P_c + P_0}{P_c} \right)^{1/3} \frac{P_S}{P_c + P_S}, \quad P_S = 3P_0 \left( \frac{P_c}{P_c + P_0} \right)^{4/3}$$

(7)
Using the expressions Equations (6) and (7) for $P_{\text{max}}$ from Equation (3) it can be written:

$$P_{\text{max}} = \frac{P_0}{81} \left(1 + \frac{P_0}{P_c}\right)^4 \left[\left(\frac{P_c}{P_0} + 3\right)\left(\frac{P_c}{P_0}\right)^{4/3}\right]^{4/3}$$

(8)

In the limit $P_m >> P_0$ and Equation (8) simplifies:

$$P_{\text{max}} = \frac{P_m}{81} \left(\frac{P_m}{P_0}\right)^3$$

(9)

Equation for bubble collapse time Equation (10), obtained by Rayleigh when considering a cavity filled with vacuum is applicable for further evaluation.

$$\tau_c = 0.915 R_{\text{max}} \sqrt{\frac{\rho_2}{P_0}}$$

(10)

Resulting expressions allow calculating the force influence of a separate collapsing cavitation element on the flat surface of a solid.

3.3. Cavitation Mechanism of Erosive Approach for Metal Oxides Dissolution in DES

The pressure on its surface can reach relatively high values during the collapse of the cavitation volume. At the same time spherical disturbances of specific amplitude are emitted in liquid generating shock waves that provide cavitation destruction of solid components. For more detailed understanding of such process, it is useful to consider a simple model of a single bubble, located near the processing surface on the distance equal to $z = L_0$. The surface itself is located in $z = 0$ along the normal to 0Z direction (Figure 3).

![Figure 3. Scheme of the spherical shock wave action to the flat surface of solid.](image)

At the moment $t = 0$ the radius of the bubble is $R_{\text{min}}$ while pressure on its surface reaches its maximum value $P_{\text{max}}$. Dotted line on Figure 3 shows the emerging spherical shock wave. Behavior of the latter can be fully described by two parameters: the density of the liquid $\rho_0$ and energy $E$ concentrated initially inside the bubble and released after collapse. Such energy in turn is determined by the expression below:

$$E = \frac{4\pi R_{\text{min}}^3}{3} P_{\text{max}}$$

(11)
By dimensional analysis one can achieve the wave propagation process description. In particular, from the abovementioned parameters and two independent variables—time \( t \) and front position (coordinate) from center \( L(t) \)—only one independent nondimensional combination can be composed:

\[
L(t) \left( \frac{\rho_0}{Et^2} \right)^{1/5} \tag{12}
\]

Its existence indicates a certain self-similarity of the process. As a result, it can be argued that the shock wave front position at every moment should match the same constant value \( \beta \) of nondimensional combination under consideration. Equation (13) represents the law of shock wave front movement from the center of the bubble over time.

\[
L(t) = \beta \left( \frac{Et^2}{\rho_0} \right)^{1/5} \tag{13}
\]

With known distance \( L_0 \) from the center of the bubble to the surface of metal oxide in the initial moment, one can define the time it takes for the wave front to reach the target using Equation (12).

While the shock wave front moves away from the center of the collapsing cavitation bubble, the pressure leap on it decreases as a result of redistribution over the surface of the sphere. It is shown on Figure 3 that on the front of the shock wave, pressure drop will be lower than the yield strength of the metal \( \sigma_T \) for \( L(t) \leq L_c \), where \( L_c \) is determined from:

\[
R_{\min}^2 L_c^2 = \frac{P_{\max}}{\sigma_T}, \quad L_c = R_{\min} \sqrt{\frac{P_{\max}}{\sigma_T}}. \tag{14}
\]

Thus, erosion goes on until reaching \( t_c \), when \( L(t_c) = L_c \). It is obvious that only bubbles that are at a distance closer than \( L_c \) from the metal oxide surface can take part in this process (i.e., \( L_0 \leq L_c \)). On the other hand, size of the forming cavity in diameter cannot exceed \( 2L_c \). If to designate the density of bubble germs, i.e., their amount in a unit of volume, as \( \kappa \), then in liquid column with a single site on a target surface and height \( \Delta L \) their number will be \( \Delta n = \kappa \Delta L \). After the collapse every bubble will create through the generated shock wave on the metal oxide surface a certain cavity, the size of which will depend on \( L_0 \) and \( L_c \). Volume \( V \) of such cavity, limited by the metal oxide surface and spherical segment with a radius \( L_c \) centered on the height \( L_0 \) from the surface of the target is determined by the following integral:

\[
V = 2\pi \int_0^{\theta_c} d\theta \sin \theta \int_{L_1}^{L_c} dr r^2, \quad \theta_c = \arccos \frac{L_0}{L_c} \quad L_1 = L_c - \frac{L_0}{\cos \theta} \tag{15}
\]

After integration expression Equation (16) is obtained:

\[
V \equiv V(L_0) = 2\pi L_c^2 L_0 \left\{ \ln \frac{L_c}{L_0} - \frac{2}{3} + \frac{L_0}{L_c} - \frac{L_0^2}{3L_c^2} \right\} \tag{16}
\]

As expected, size of the cavity depends on height \( L_0 \) under the surface of metal oxide at which the germ has appeared. In the column of liquid with the height \( \Delta L_0 \) and a unitary base (by area) there are \( \kappa \Delta L_0 \) of germs that create cavities of total volume \( \Delta V \), which can be calculated using Equation (17):

\[
\Delta V = 2\pi L_c^2 L_0 \kappa \left\{ \ln \frac{L_c}{L_0} - \frac{2}{3} + \frac{L_0}{L_c} - \frac{L_0^2}{3L_c^2} \right\} \Delta L_0 \tag{17}
\]

Integration of Equation (17) over all values of \( L_0 \) leading to cavity formation (i.e., in the range \( 0 \leq L_0 \leq L_c \)) allows one to define the total volume of the cavities produced
by cavitation. Knowledge of the density of metal oxide $\rho_M$ is useful for eroded material mass calculation:

$$M = \frac{5}{6} \pi L^4 \alpha_\kappa \rho_M$$

(18)

Here $S$ is the total surface area of the processed metal oxide. Mass $M$ determined according to Equation (18) is released during the time lower than a quarter of ultrasound oscillation period at the moment when the period of rarefaction is over, and compression begins [37]. During $N$ periods it increases by $N$ times, i.e., it grows linearly with time accurate to oscillation period $T = \frac{2\pi}{\omega}$ so for the total mass it can be written:

$$M_T = M_T^\tau = \frac{5}{12} \left( \frac{P_m}{P_0} \right)^4 \left( \frac{P_0}{\alpha_T} \right)^2 R^4 \alpha_\kappa \rho_M \omega \tau$$

(19)

where $\tau$—current time, whose unit exceeds the period of ultrasonic oscillations $T$. The linear dependence of the dissolved metal oxide mass on time can be observed only in case of ideal conditions, compliance of which is necessary to ensure the correctness of the calculations performed within this model. In practice it can be very difficult to achieve. For example, the homogeneous distribution of the cavitation bubbles can be easily disturbed both by side fluid flows and by the ultrasonic cavitation excitation features. The particle sizes of the eroded metal oxide can also vary due to many different reasons. Therefore, corresponding dependencies cannot be perfectly linear. At the same time even in case of such deviations a near-linear trend should be observed. From Equation (19) one can see that mass of eroding metal oxide is highly sensible even to small changes of acoustic pressure.

It is noteworthy that using expression Equation (10) it is possible to determine the time of collapse. In case it is much longer than the period of US oscillations, the efficiency of erosion caused by cavitation will be significantly lower. It is also important that $\kappa$ value not only characterizes the liquid itself, but its condition. The point is that it is very difficult to create a cavity (i.e., to destroy continuous medium) in an ideal liquid: extremely high acoustic pressure is needed. But real liquid contains a lot of impurities, gas bubbles and micro particles. Structure on such boundaries differs from the ideal case, and hence there is an opportunity for cavity germs generation and growth during oscillating acoustic pressure extension. Thus, even the same liquid can be characterized by different values of $\kappa$ in various conditions according to this model.

Touching the surface of metal oxide solvent molecules (DES components) suffer collisions with atoms located in lattice sites with collision frequency $v_\tau$. If the temperature of liquid and, respectively, the kinetic speed $v_T$ of solvent molecules is high enough then together with the chemical adhesion forces it is possible to overcome the energy barrier holding metal atom in lattice and to transfer atom in solution (i.e., to dissolve it). Therefore, for the time of about collision duration $\tau_c = \frac{1}{v_a}$ thin layer of saturated metal solution is formed near the surface. It prevents further fast dissolution of the material under DES influence. Destruction of such a layer will promote the dissolution process, but it occurs only with a low rate of thermal drift $v_d$. In the presence of additional streams capable of breaking the layer on the metal oxide surface, the dissolution process intensifies.

Usage of ultrasound that supports the cavitation erosion process allows boosting the metal oxide dissolution in deep eutectic solvent by action of several factors. Firstly, it promotes shredding of solid, which significantly increases the area of surface in contact with DES, i.e., many more molecules are transferred into solution. Secondly, US is able to create micro flows that provide comparably fast inflow of fresh portions of DES to metal oxide surface, which also speeds up the dissolution.

It is possible to evaluate the mass of solid transferred into solution $M_0$ during the time comparable to the interval between collisions of solvent molecules $\tau_c$ if to assume that saturated solution on the border with DES is formed during the same time. Considering
that section of contact of interacting mediums is a rectangle with area of \( S \) it is fair to write the following expression for \( M_0 \):

\[
M_0 = \rho_M S^2 C_a \tau_c v_T h_c \mu_c
\]  

(20)

Here \( C_a \)—solvent concentration, \( h_c \)—metal oxide crystal lattice constant (distance between atoms), \( \mu_c \)—coefficient, associated with chemical activity of interaction between DES and metal oxide.

In case the time between collisions of particles is significantly lower than time needed for area \( S \) crossing (with drift speed \( v_d \)) along its direction it can be postulated that during time equal to \( \sqrt{S/v_d} \) the value of \( M_0 \) will not practically change since the solution has already reached its maximum concentration. So \( \Delta\tau = \sqrt{S/v_d} \) is a minimal time period for which the mass of dissolved oxide increases by \( \Delta m = M_0 \). Hence the rate of dissolution (or metal oxide mass growth in DES) is equal to:

\[
\frac{\Delta m}{\Delta\tau} = \frac{dm}{d\tau} = \frac{M_0 v_d}{\sqrt{S}} = \rho_M S^{3/2} C_a \frac{v_S v_T}{v} h_c \mu_c
\]  

(21)

It is clear that mass of dissolved oxide grows linearly with time.

As \( v \sim T \) and \( v_T \sim T^{1/2} \) this rate is at least proportional to \( T^{3/2} \) because \( h_c, \mu_c \) and \( v_d \) can also be temperature dependent. This to a certain extent correlates with experimental results obtained earlier in our group for two different temperatures of used acid [22].

In case the removal of near-surface layer (saturated solution) occurs with assistance of external flows, for example, due to stirring, acoustic flows, drains then corresponding expression for rate should be placed instead of \( v_d \). However, in case of cavitation erosion the obtained value of mass of dissolving metal oxide will not match the real situation. The thing is that besides the updating metal oxide surface there is a whole mass of produced metallic powder that also interacts with DES. Hence it is necessary to include in Equation (21) an additional term that is equal to \( dM_t/d\tau \) Equation (18) to take into account the contribution of powder dissolution. As a result, for ultrasound assistance the following expression is obtained:

\[
\frac{dm}{d\tau} = \rho_M S \left\{ \left( \frac{P_m}{P_0} \right)^3 \left( \frac{P_0}{\rho_0} \right)^{3/2} \frac{R_i \kappa \omega}{\sqrt{S}} \frac{v_S v_T}{v} h_c \mu_c + \sqrt{S} C_a \frac{v_S v_T}{v} h_c \mu_c \right\}
\]

(22)

where \( v_S \) is an acoustic micro flows rate that according to literature is close to the value presented below:

\[
v_S \approx \frac{1}{5} \frac{P_m^2}{\rho_0 c_0^3}
\]

(23)

where \( c_0 \) is the speed of sound in liquid and \( \rho_0 \)—density of the latter.

One can see from Equation (22) that behavior of eroding and dissolving metals in time (normalized for its entire amount) is described by linear dependence. Intensification of processes induced by operations with several parameters can lead only to slope variation, i.e., to rate change. It is noteworthy that without ultrasonic assistance the process of dissolution can last much longer.

At the same time, it is interesting to evaluate the influence of ultrasound on quantitative parameters of cavitation erosion and dissolution of metal oxide in different practical situations. Figure 4 illustrates the dependence of metallic powder mass, formed by cavitation erosion over a fixed period of ultrasonic treatment on ultrasonic intensity.
Figure 4. Dependence of metal oxide powder mass on ultrasound intensity for the same period of processing (normalized form): 1—mass of metal oxide dissolved in efficient US erosion conditions; 2—amount of metal oxide shredded by US erosion; 3—dissolution of metal oxide in the absence of eroded particles.

It can also be seen that for the same time there is much more dissolved metal oxide since in the absence of obstacles (fast powder conglomeration, their transfer to saturated solution zone, etc.) metal oxide particles are also transferred to solution from the surface, which was treated with cavitation and fully prepared for interaction with solvent. In the case when erosion is suppressed (curve 3—metal oxide is outside the cavitation zone, the intensity of ultrasound is below its threshold value, etc.), dissolution is significantly slower and does not increase as quickly with an increase in the intensity of ultrasound, as in the case of complete connection of cavitation to the extraction process, when, due to the increase in ultrasound power, the number of cavitation bubbles increases, the mass of the eroded metal becomes larger and curves 2 and 3 intersect.

Ultrasound can affect the course of many chemical processes, including, for example, the physical kinetics of metal oxide dissolution reactions in DES. However, the peculiarities of its influence on each of them are more accurately and reliably studied in the case when the influence of others is small and can be neglected. In this paper, the phenomenon of ultrasonic erosion dissolution of metal compounds is considered in conditions when other chemical reactions have no significant influence. The criterion of correctness of theoretical conclusions is the experimental confirmation of obtained results realized in correctly chosen conditions of corresponding experiment. At the same time, it should be noted that the acceleration of other processes associated with ultrasound can distort the dissolution pattern compared to the case where the intensification is associated only with an increase in the interaction surface of the reagents. But it does not affect the realization of this process.

4. Results and Discussion

Mechanistic study of the ultrasonic influence on the dissolution of metal oxides in DES is complicated because it simultaneously affects different aspects of the process. Firstly, ultrasonic erosion causes the total surface area to increase by shredding the material, which results in reaction speed acceleration. Secondly, US-generated acoustic currents, micro
flows, and vibrations of the fluid promote the dissolution by removing the saturated solution and replacing it with fresh near the phase contact (i.e., by mixing). Finally, acoustic pressure oscillations make solvent particles move intensively, which in turn increases its dissolving ability and leads to the reaction kinetics changing. When all these features affect the dissolution equally it is very difficult to identify the contribution of each. Therefore, it is worth studying them separately. The main difficulty in practice is the selection of such experimental conditions when only one of the aforementioned contributions affects the process while the influence of the others can be neglected. The present research is primarily devoted to a theoretical description of the impact of ultrasonic cavitation erosion on dissolution of metal oxides in DES. For this, we used several assumptions based on the understanding of the physical nature of the processes under study. Their mathematical justification occupies much space and is not always entirely convincing. Therefore, corresponding experiments were carried out for the confirmation of the correctness of the used approximations.

We obtained the experimental data on kinetics of dissolution of CoO, Ni$_2$O$_3$ and Mn$_2$O$_3$ in choline chloride/sulfosalicylic acid (7:3) as a deep eutectic solvent. Comparative analysis of theoretical and experimental results in US and non-US conditions was carried out. Figure 5 shows that US significantly increased the dissolution rate of metal oxides in DES. The tendency to increase the metal content in DES when using ultrasound was observed for all the metal oxides under study. In the case of manganese (III) oxide, equilibrium was reached in 40 min (instead of 90 min) due to the effect of ultrasound. For Ni$_2$O$_3$ at 60 min an increase of the metal content in DES up to 28 wt% was observed (against 4.5 wt%), while in the case of CoO metal content increases from 45 to 80 wt% after 10 min of the experiment with the US usage.

![Figure 5. Cont.](image)
Figure 5. Metal oxides dissolution kinetics (Mn(III)—(a), Ni(III)—(b), Co(II)—(c) in choline chloride/sulfosalicylic acid (7:3) as a deep eutectic solvent: lines—theory, markers—experiment.

The theoretical curves in Figure 5 that represent the corresponding function proportional to $M_0(\tau)$ according to relationship (19) were obtained for the ultrasound amplitude $P_m = 0.4 \, \text{MPa}$ and the following parameters of the liquid: $\alpha = 0.075 \, \text{kg/s}$, $\kappa = 10^{21} \, \text{m}^{-3}$, $\rho_M = 8 \times 10^{-3} \, \text{kg/m}^3$, $\omega = 35 \, \text{kHz}$, $P_0 = 0.1 \, \text{MPa}$, $P_g = 0.01 \, \text{MPa}$ and $S = 1.5 \times 10^{-4} \, \text{m}^2$. As one can see, experimental data correlates well with theoretical calculations, which confirms the correctness of the developing picture about the physicochemical nature of the metal oxide dissolution in DES. Simultaneous operation of several US-caused aspects accelerating the dissolution (e.g., direct effect on the kinetics) leads to distortions not observable in the case of exclusive erosive cavitation contribution. Apparently, such a case is shown in Figure 5b. However, its detailed analysis and identification of the reasons for the discrepancy between theory and experiment is the subject for an independent large-scale study on the direct effect of ultrasound on the kinetics of dissolution.
It is also worth noting that strong deviation from an optimal working regime (excessive erosion boost causing powder particles conglomeration due to the fact they have not enough time for dissolution and hence overall process deceleration or superfast oxide metal surface processing with special flow generation) can change the linear character of dissolved metal mass–time dependence, but consideration of such cases lies outside the area of interest of practical use of ultrasonic leaching technology.

5. Conclusions

Technology of metal leaching from solid components includes several stages such as dissolution of valuable raw material and its following extraction from the solution, i.e., it is a multistep process. It is also applied in the case of US-assisted leaching systems, and so there are some specific features about functioning of similar technologies, among which the most important are:

1. Efficient intensification of leaching cannot be achieved simply by acceleration of every step. Due to synchronism of some processes, it is necessary to set the operating regime in such a way that different stages do not interfere with each other and moreover provide the best conditions for the entire process realization. For example, accumulation of powder that is too fast prevents efficient dissolution due to formation of conglomerates; therefore, consistency of parameters should take this feature of the process into account;

2. Ultrasound is able to boost the dissolution of metal oxide not only by its shredding (cavitation-induced) but also by creating an acoustic flow that promptly deletes the saturated solution film (interfering fast metal oxide molecules transfer) from the surface. Specific organization of such a process helps to significantly increase the efficiency of mentioned technology. However, the search for the key features and determination of optimal conditions requires additional independent study. It may result in new intriguing and practically useful recommendations and engineering solutions. In addition, results obtained during this research allow evaluating the value of flow rate in liquid. Considering the scope of mentioned schemes, including of such additional flow sources can boost the dissolution process;

3. Diversity of configurations in the area of cavitation and the abundance of methods of ultrasound usage for their generation allows choosing the most efficient variant for every specific scheme. It is extremely important for maximal process intensification achievement. At the same time, one can use different types of waves, products of their interaction and features of nonlinear US modification. The latter include solitary acoustic impulses, self-focusing US beams, and nonlinear wave structures. It is possible to develop new or to modify old leaching systems with their help;

4. It was found that ultrasound allows intensifying the dissolution process of Mn(III), Ni(III), and Co(II) oxides in DES choline chloride/sulfosalicylic acid (7:3). The experimental data correlate well with the theory. This fact allows us to speak about the adequacy of the proposed theoretical calculations describing kinetics of metal oxides dissolution process in DES.

Author Contributions: Conceptualization, O.M.G. and A.A.V.; methodology, O.M.G. and A.A.V.; software, O.M.G.; validation, O.M.G., Y.A.Z. and A.A.V.; formal analysis, Y.A.Z.; investigation, I.V.Z.; resources, O.M.G.; data curation, Y.A.Z.; writing—original draft preparation, O.M.G. and I.V.Z.; writing—review and editing, Y.A.Z. and A.A.V.; visualization, I.V.Z.; supervision, Y.A.Z. and A.A.V.; project administration, A.A.V.; funding acquisition, A.A.V. All authors have read and agreed to the published version of the manuscript.

Funding: The study was carried out at the expense of the grant of the Russian Scientific Fund (Project No. 20-13-00387).

Conflicts of Interest: The authors declare no conflict of interest.
References

1. Sandiluya, D.K.; Kannan, A. Intensification of the Dissolution of a Sparingly Soluble Solid from a Spinning Disk in the Presence of Power Ultrasound. *Ind. Eng. Chem. Res.* **2011**, *50*, 13083–13091. [CrossRef]

2. Narayana, K.L.; Swamy, K.M.; Rao, K.S.; Murty, J.S. Leaching of Metals from Ores with Ultrasound. *Miner. Process. Extr. Metall. Rev.* **1997**, *16*, 239–259. [CrossRef]

3. Golmohammadzadeh, R.; Faraji, F.; Rashchi, F. Recovery of lithium and cobalt from spent lithium-ion batteries (LIBs) using organic acids as leaching reagents: A review. *Resour. Conserv. Recycl.* **2018**, *136*, 418–435. [CrossRef]

4. Gui, Q.; Khan, M.I.; Wang, S.; Zhang, L. The ultrasound leaching kinetics of gold in the thiosulfate leaching process catalysed by cobalt ammonia. *Hydrometallurgy* **2020**, *196*, 105426. [CrossRef]

5. Wang, X.; Srinivasakannan, C.; Duan, X.-h.; Peng, J.-h.; Yang, D.-j.; Ju, S.-h. Leaching kinetics of zinc residues augmented with ultrasound. *Sep. Purif. Tech.* **2013**, *115*, 66–72.

6. Avvaru, B.; Roy, S.B.; Chowdhury, S.; Hareendran, K.N.; Pandit, A.B. Enhancement of the Leaching Rate of Uranium in the Presence of Ultrasound. *Ind. Eng. Chem. Res.* **2006**, *45*, 7639–7648. [CrossRef]

7. Rao, K.S.; Narayana, K.L.; Swamy, K.M.; Murty, J.S. Influence of ultrasound in ammoniacal leaching of a copper oxide ore. *Metall. Mater. Trans B* **1997**, *28*, 721–723. [CrossRef]

8. Li, X.; Zhang, J.; Yang, D. Determination of Antiscalcing Efficiency and Dissolution Capacity for Calcium Carbonate with Ultrasonic Irradiation. *Ind. Eng. Chem. Res.* **2012**, *51*, 9266–9274. [CrossRef]

9. Gradov, O.M.; Voshkin, A.A.; Zakodyayaeva, Y.A. Estimating the parameters of ultrasonically induced mass transfer and flow of liquids in the pseudomembrane method. *Chem. Eng. Process. Process Intensif.* **2017**, *118*, 54–61. [CrossRef]

10. Gradov, O.M.; Voshkin, A.A.; Zakodyayaeva, Y.A. Analysis of the possible applications of the acoustic flow effect for the breakup and transfer of liquid substances in a cylindrical volume. *Theor. Found. Chem. Eng.* **2017**, *51*, 876–882. [CrossRef]

11. Gradov, O.M.; Zakodyayaeva, Y.A.; Voshkin, A.A. Breakup of immiscible liquids at the interface using high-power acoustic pulses. *Chem. Eng. Process. Process Intensif.* **2018**, *125*, 133–140. [CrossRef]

12. Gradov, O.M.; Zakodyayaeva, Y.A.; Zinov’eva, I.V.; Voshkin, A.A. Some Features of the Ultrasonic Liquid Extraction of Metal Ions. *Molecules* **2019**, *24*, 3549. [CrossRef]

13. Gradov, O.M.; Zakodyayaeva, Y.A.; Zinov’eva, I.V.; Voshkin, A.A. Ultrasonic Intensification of Mass Transfer in Organic Acid Extraction. *Processes* **2021**, *9*, 15. [CrossRef]

14. Gradov, O.M.; Zakodyayaeva, Y.A.; Voshkin, A.A. Dynamics of Mass Transfer through the Interface between Immiscible Liquids under the Resonance Effect of Ultrasound. *Theor. Found. Chem. Eng.* **2020**, *54*, 1148–1155. [CrossRef]

15. Xiao, J.; Yuan, J.; Tian, Z.; Yang, K.; Yao, Z.; Yu, B.; Zhang, L. Comparison of ultrasound-assisted and traditional caustic leaching of spent cathode carbon (SCC) from aluminum electrolysis. *Ultrason. Sonochem.* **2018**, *40*, 21–29. [CrossRef]

16. Karami, E.; Kuhar, L.; Bona, A.; Nikoloski, A.N. A review of electrokinetic, ultrasonic and solution pulsing methods for mass transfer enhancement in in-situ processes. *Minerals Eng.* **2021**, *170*, 107029. [CrossRef]

17. Lei, C.; Aldous, I.; Hartley, J.M.; Thompson, D.L.; Scott, S.; Hanson, R.; Anderson, P.A.; Kendrick, E.; Sommerville, R.; Ryder, K.S.; et al. Lithium ion battery recycling using high-intensity ultrasonication. *Green Chem.* **2021**, *23*, 4710. [CrossRef]

18. Marafi, M.; Stanislaus, A. Waste Catalyst Utilization: Extraction of Valuable Metals from Spent Hydroprocessing Catalysts by Ultrasonic-Assisted Leaching with Acids. *Ind. Eng. Chem. Res.* **2011**, *50*, 9495–9501. [CrossRef]

19. Kong, J.; Xing, P.; Wei, D.; Zhuang, Y. Ultrasound-Assisted Leaching of Iron from Silicon Diamond-Wire Saw Cutting Waste. *JOM* **2021**, *73*, 791–800. [CrossRef]

20. Li, H.; Eksteen, J.; Oraby, E. Hydrometallurgical recovery of metals from waste printed circuit boards (WPCBs): Current status and perspectives—A review. *Resour. Conserv. Recycl.* **2018**, *139*, 122–139. [CrossRef]

21. Sun, Z.; Cao, H.; Xiao, Y.; Sietsma, J.; Jin, W.; Agterhuis, H.; Yang, Y. Toward Sustainability for Recovery of Critical Metals from Electronic Waste: The Hydrochemistry Processes. *ACS Sust. Chem. Eng.* **2019**, *7*, 5040–5053. [CrossRef]

22. Fedorova, M.I.; Zakodyayaeva, Y.A.; Baranchikov, A.E.; Kreny, V.A.; Voshkin, A.A. Extraction Reprocessing of Fe, Ni-Containing Parts of Ni–MH Batteries. *Russ. J. Inorg. Chem.* **2021**, *66*, 266–272. [CrossRef]

23. Zakhodyaeva, Y.A.; Izyumova, K.V.; Solov’Eva, M.S.; Voshkin, A.A. Extraction separation of the components of leach liquors of batteries. *Theor. Found. Chem. Eng.* **2017**, *51*, 883–887. [CrossRef]

24. Alvial-Hein, G.; Mahandra, H.; Gahreman, A. Separation and recovery of cobalt and nickel from end of life products via solvent extraction technique: A review. *J. Clean. Prod.* **2021**, *297*, 126992. [CrossRef]

25. Thompson, D.L.; Hartley, J.M.; Lambert, S.M.; Shiref, M.; Harper, G.D.J.; Kendrick, E.; Anderson, P.; Ryder, K.S.; Gains, L.; Abbott, A.P. The importance of design in lithium ion battery recycling—A critical review. *Green Chem.* **2020**, *22*, 7585. [CrossRef]

26. Richter, J.; Ruck, M. Synthesis and Dissolution of Metal Oxides in Ionic liquids and Deep Eutectic Solvents. *Molecules* **2019**, *25*, 78. [CrossRef]

27. Zürner, P.; Frisch, G. Leaching and selective extraction of indium and tin from zinc flue dust using an oxalic acid based deep eutectic solvent. *ACS Sust. Chem. Eng.* **2019**, *7*, 5300–5308. [CrossRef]

28. Hansen, B.B.; Spittle, S.; Chen, B.; Poe, D.; Zhang, Y.; Klein, J.M.; Horton, A.; Adhikari, L.; Zelovich, T.; Doherty, B.W.; et al. Deep eutectic solvents: A review of fundamentals and applications. *Chem. Rev.* **2021**, *121*, 1232–1285. [CrossRef]

29. Abbott, A.P.; Capper, G.; Davies, D.L.; McKenzie, K.J.; Obi, S.U. Solubility of Metal Oxides in Deep Eutectic Solvents Based on Choline Chloride. *J. Chem. Eng. Data.* **2006**, *51*, 1280. [CrossRef]
30. Pateli, I.M.; Thompson, D.; Alabdullah, S.; Abbott, A.P.; Jenkin, G.; Hartley, J. The effect of pH and hydrogen bond donor on the dissolution of metal oxides in deep eutectic solvents. *Green Chem.* **2019**, *22*, 5476. [CrossRef]

31. Macchioni, V.; Carbone, K.; Cataldo, A.; Fraschini, R.; Bellucci, S. Lactic acid-based deep eutectic solvents for the extraction of bioactive metabolites of *Humulus lupulus* L.: Supramolecular organization, phytochemical profiling and biological activity. *Sep. Purif. Technol.* **2021**, *264*, 118039. [CrossRef]

32. Lakka, A.; Karageorgou, I.; Kaltsa, O.; Batra, G.; Bozinou, E.; Lalas, S.; Makris, D. Polyphenol Extraction from *Humulus lupulus* (Hop) Using a Neoteric Glycerol/L-Alanine Deep Eutectic Solvent: Optimisation, Kinetics and the Effect of Ultrasound-Assisted Pretreatment. *AgricEng*ering **2019**, *1*, 30. [CrossRef]

33. Wang, X.; Wu, Y.; Li, J.; Wang, A.; Li, G.; Ren, X.; Yin, W. Ultrasound-assisted deep eutectic solvent extraction of echinacoside and oleuropein from Syringa pubescens Turcz. *Ind. Crops Prod.* **2020**, *151*, 112442. [CrossRef]

34. Schaeffer, N.; Passos, H.; Gras, M.; Rodriguez Vargas, S.J.; Neves, M.C.; Svecova, L.; Papaiconomou, N.; Coutinho, J.A.P. Selective separation of manganese, cobalt and nickel in a fully aqueous system. *ACS Sustain. Chem. Eng.* **2020**, *8*, 12260–12269. [CrossRef]

35. Zinov’eva, I.V.; Fedorova, A.Y.; Milevskii, N.A.; Zakhodyaeva, Y.A.; Voshkin, A.A. A Deep Eutectic Solvent Based on Choline Chloride and Sulfosalicylic Acid: Properties and Applications. *Theor. Found. Chem. Eng.* **2021**, *55*, 371–379. [CrossRef]

36. Ivanov, A.V.; Figurovskaya, V.N.; Ivanov, V.M. Molecular absorption spectroscopy of 4-(2-pyridilazo)resorcinolcomplexes as alternative for the atomic absorption spectroscopy. *Mosc. Univ. Chem. Bull.* **1992**, *33*, 570–574.

37. Flynn, H.G. Physics of acoustic cavitation in liquids. In *Physical Acoustics*; Mason, W.P., Ed.; John Wiley & Sons: New York, NY, USA, 1964; Volume 16, pp. 57–172.