Ultrasound pretreatment of elemental iron: kinetic studies of dehalogenation reaction enhancement and surface effects

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Abstract

This work presents data showing the kinetic improvement afforded by ultrasound pretreatment and illustrates the physical and chemical changes that take place at the iron surface. First-order rate constants improved as much as 78% with 2 h of ultrasound pretreatment. Scanning electron microscopy (SEM) and surface area analysis were used for confirmation of the physical changes that take place after ultrasound was used on iron surfaces exposed to a variety of conditions. X-ray photoelectron spectroscopy was used to determine chemical surface characteristics before and after ultrasound use. SEM and surface area analysis showed that ultrasound use clears the iron surface of debris increasing the surface area up to 169%. In addition, exposure to ultrasound alters ratios of surface species, such as adventitious carbon to carbonyl carbon and iron to oxygen, and removed hydroxides thus making the iron more reactive to reductive dehalogenation.

Keywords: Trichloroethylene; Iron; Ultrasound; Groundwater remediation

1. Introduction

During the past decade, the use of permeable reactive barriers (PRBs) has shown great promise for the in situ remediation of groundwater contaminated with chlorinated solvents. Environmental conditions encourage a surface layer of corrosion products to develop due to the thermodynamic instability of Fe0 in the presence of water [1]. Several researchers have found that a reduction in dechlorination rates and decreased flow through the treatment areas can be linked to chemical deposition of material [2-4]. Batch and column studies have shown that the corrosion products are a complex mixture of amorphous iron oxides, iron oxide salts, and other mineral precipitates [5-7]. Mackenzie et al. [4] found that hydroxides can cause reduced porosity early in treatment periods while hydroxides and carbonates cause reduction in flow over longer treatment periods. Bridging between iron particles can result in plugged pore spaces at the upstream face of a barrier and interfere with the hydraulics of a remediation system [8]. Porosity losses and reduced flow can also be expected in the bulk iron material caused by mineral precipitation [4]. The extent of surface passivation has been found to be dependent not only on TCE concentration but also on groundwater electrolyte concentrations [9]. Chloride and sulfate containing waters caused an increase in half-life from 400 to 2500 min after 657 days. Nitrate containing waters caused even slower half-lives [9]. In an aquifer with significant alkalinity, and especially under even slight aerobic conditions, eventual passivation of the iron surface and reduced reactivity are inevitable. These problems are likely to occur first at the upstream portion of the permeable barrier, where the greatest contaminant mass transfer takes place.

Ultrasound has been studied for direct degradation of chlorinated solvents [10] and also in conjunction with iron [11]. Geiger et al. [12] studied the TCE/iron/...
ultrasound system and found enhanced rate constants for the disappearance of TCE. Hung and Hoffmann [11] found that the continuous use of ultrasound in the presence of iron increased the rate constants for the degradation of carbon tetrachloride by a factor of 40. Research has shown that surface defects and abnormalities increase the percentage of active sites on the iron surface [13]. Ultrasound causes pitting and cracking of many metal surfaces thus increasing the degradation reaction rates [14] and should remove corrosion products at least down to a thin layer of oxide. A thin oxide layer is capable of acting as a semiconductor for electron transfer or as a coordination site for electron transfer through \( \text{Fe}^{2+}/\text{Fe}^{3+} \) species [1]. Improved efficiency and increased activity due to surface changes created by sonication have also been noted in lithium [15], zinc [16], and copper catalysts [17].

Although the most common uses of ultrasound involve cleaning surfaces in an aqueous environment, experiments that have been reported show that ultrasonic energy can pass through water saturated soil in energy levels adequate to clean an iron surface to a distance of 54 cm [18].

These findings and the results of the work presented in this paper show that there is a reason to pursue ultrasound as a methodology for restoring the efficiency of iron containing PRBs.

2. Experimental section

Reagents (at least 99% pure) were obtained from Fisher Scientific and were used as received. Coarse uncrushed iron filings were obtained from Peerless Corporation (Cincinnati, OH). One hundred-mesh iron powder was obtained from Mallinckrodt Chemicals (Paris, KY 40361). One-liter Tedlar® gas sampling bags with dual-function, septum/side-valve sampling ports were obtained from SKC (Dallas, TX). Natural groundwater was obtained from the East Coast of Central Florida.

2.1. Procedure

Each experiment consisted of four (two duplicate sets) 1.0-L Tedlar® bags of identically processed iron which received different amounts of ultrasound. Each bag contained 25 g of iron, measured prior to any treatment, loaded with 500 mL of natural groundwater, and immediately purged with nitrogen gas for 30 min then evacuated to zero head space. The bag was then either sonicated for 2 h (330 Wh) or immediately dosed with a stock aqueous solution to yield a TCE concentration of approximately 14 mg/L. A 600 W, 20 kHz Branson Ultrasonic water bath was used for sonication. After dosing, the bags were placed on a shaker table set at a rate of 160 shakes per minute, to ensure adequate mixing and remained at ambient conditions, about 22°C, throughout a 28-day experiment.

2.2. Iron treatment

Iron was used as received (unwashed), treated with an acid wash or intentionally oxidized. The acid wash consisted of immersing the iron in 5% sulfuric acid for 2 min and three consecutive rinses with deionized water. The intentionally oxidized iron was first acid washed then allowed to oxidize under ambient conditions for 21 days. To further study the effect of sonication on deteriorated iron, a column from an associated study was sacrificed after treating more than 300 pore volumes of unbuffered solution with TCE concentrations of 14 mg/L. The reactive material was composed of 20% acid-washed iron filings and 80% coarse sand, by weight. Material retrieved from the entrance end of the column was placed in bags at a level of 125 g (80% sand, 20% iron) per bag, to yield 25 g of iron per bag.

2.3. Groundwater chemistry

Major physical and chemical properties of the natural groundwater used in this study are summarized in Table 1. “Field” indicates parameters which were measured with a Corning Checkmate M90 field instrument with interchangeable probes. The groundwater is distinguished by significant hardness (444 mg/L as CaCO₃) and alkalinity (289 mg/L as CaCO₃).

2.4. Sample collection

Single samples were removed via a side valve on the bag septum using a gas-tight syringe and placed into 12-mL glass vials with Teflon-lined septa screw caps (zero head space). The sample vials were then wrapped with parafilm and immediately refrigerated at 4°C until analyzed.

Table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
<th>Method</th>
</tr>
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<tr>
<td>pH</td>
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<td>—</td>
<td>Field</td>
</tr>
<tr>
<td>Dissolved oxygen</td>
<td>0.1</td>
<td>mg/L</td>
<td>Field</td>
</tr>
<tr>
<td>Conductivity</td>
<td>1923</td>
<td>μS</td>
<td>Field</td>
</tr>
<tr>
<td>Ca</td>
<td>81.4</td>
<td>mg/L</td>
<td>EPA 6010</td>
</tr>
<tr>
<td>Mg</td>
<td>57.7</td>
<td>mg/L</td>
<td>EPA 6010</td>
</tr>
<tr>
<td>Fe</td>
<td>0.059</td>
<td>mg/L</td>
<td>EPA 6010</td>
</tr>
<tr>
<td>Hardness</td>
<td>444</td>
<td>mg/L as CaCO₃</td>
<td>EPA 130</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>71</td>
<td>mg/L</td>
<td>EPA 300</td>
</tr>
<tr>
<td>Total alkalinity</td>
<td>289</td>
<td>mg/L as CaCO₃</td>
<td>EPA 310.1</td>
</tr>
<tr>
<td>Total dissolved solids</td>
<td>1100 mg/L</td>
<td>EPA 160.1</td>
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</tbody>
</table>
A small amount of head space that evolved over time in some experiments was sampled by using a 1.0 mL gas-tight syringe (Hamilton) through the septum port of the bag. The bubble of head space was removed in this manner at the conclusion of the experiment. The volume of the gas was recorded and the sample was then analyzed by gas chromatography.

2.5. Organic analysis

Liquid samples were analyzed for TCE and daughter products (dichloroethene isomers, vinyl chloride, and ethene) following EPA Method 624. A 5 mL portion was injected with 1.0 μL of internal standard (5000 mg/L bromochloromethane in methanol) then transferred to a purge vial. A Hewlett-Packard gas chromatograph Model 5890, equipped with a flame-ionization detector (FID) and a 0.25 mm i.d., 60-m long Vocol capillary column, was programmed for a 3 min hold at 60°C, a 15°C/min ramp rate to 180°C, and a 3-min hold at this final temperature.

Gas samples were analyzed using a Perkin Elmer 5800 GC equipped with an FID. The column used was a 10% carbowax packed column, 6 ft long with 1/8 in diameter, purchased through Supelco. Oven temperature was isothermal at 35°C for 30 min and the nitrogen flow rate was 10.0 mL/min.

2.6. Specific surface area

Iron powder and filings were analyzed for specific surface area before and after sonication. Samples were rinsed with acetone and dried with nitrogen. To prevent oxidation, all samples were stored under nitrogen in screw-cap, glass vials, wrapped in parafilm. Measurements were taken using a Porous Materials Inc. (PMI) Brunauer–Emmett Teller (BET) Sorptometer Model 201 (Ithaca, NY) using nitrogen as the adsorbate.

2.7. Scanning electron micrographs (SEM)

The morphology of the iron surface and deposits before and after sonication were examined via SEM. Samples were prepared with a gold-palladium mixture applied using a Hummer VI-A Sputtering System (EM Corporation, Chestnut Hill, MA) with an argon plasma and then observed with an Amray 1810 Scanning Electron Microscope (Bedford, MA).

2.8. X-ray photoelectron spectroscopy/electron spectroscopy for chemical analysis (XPS/ESCA)

XPS/ESCA studies were done using a Perkin Elmer (Norwalk, CT) PHI 5400 XPS system. These analyses were performed using aluminum Kα radiation of 350 W. Pass energies for the survey and narrow scans were 44.75 and 35 eV, respectively. All binding energies were referenced against the nonreactive adventitious C (1s) peak at 284.6 eV. A 50° take-off angle between the sample surface and analyzer entrance was used for all samples. Determining peak heights (assuming a Shirley background model) to develop full-width half-maximum (FWHM) information [19] was used for quantification.

3. Results and discussion

3.1. Effect of ultrasound on TCE concentration

In order to study the effects of ultrasound on the enhancement of iron for the degradation of TCE, the impact of ultrasound on TCE alone also had to be determined. A pair of iron blank bags were prepared and then exposed to ultrasound for up to 3 h with samples taken at 30 min, 1, 2, and 3 h. Solution TCE concentrations declined from 10.0 mg/L to slightly less than 8 mg/L (± 0.15 mg/L) but the decline in solution concentration was attributed to volatilization and this hypothesis is supported by the formation of a small (approximately 170–200 μL) gas bubble in the bags.

The only by-product formation observed (in solution or gas phase) was 1,1-DCE (1.0-ug/L) from the analysis of solution samples taken at 3 h. While other researchers have used ultrasound at higher energy levels to degrade chlorinated organics [11], that effect was not otherwise observed in this experiment due to the limited application of ultrasonic energy.

The experiment was continued for 2 weeks with no further ultrasound treatment and the loss of TCE from the Tedlar® bags was minimal with 98% (+0.3%) of the TCE accounted for in the solution and gas-phase. This indicated that there was no significant loss of TCE through the bags under the conditions used for this work.

3.2. Impact of exposure time on rate constants

Four sets of bags (loaded with deoxygenated water and iron filings previously used for a column study) were exposed to ultrasound for 0.5, 1, 2 and 3 h. TCE was then added and the bags were allowed to equilibrate for 24 h before rate studies were performed. It was found that even 0.5 h of ultrasound exposure yields some increase in TCE degradation rate constants. A significant increase in rate constants occurred when the duration of ultrasound exposure was increased to 1 h with only a slight increase beyond that exposure time (Fig. 1). Based on this study, it was concluded that the major effects of ultrasound pretreatment take place within the first hour (at this energy level).

The finding that even 30 min of ultrasound treatment improves TCE degradation rate constants supports
previous work describing possible mechanisms of electron transfer through thin oxide layers. The iron filings were heavily coated with corrosion products (based on visual observation, SEMs and XPS data) which acts to passivate the dehalogenation reaction at the surface. Brief periods of even low energy ultrasound serve to knock away some of the more loosely held debris. This exposes a reactive iron surface through pitting (causing discrete increases in dehalogenation reactions) and a thin oxide layer which has been shown to allow for electron transfer reactions [20,21].

3.3. Impact of type and condition of iron

Table 2 summarizes average first-order rate constants and surface area data for sonicated and unsonicated iron under various conditions. Rate constants were calculated after 24 h of exposure to TCE to allow equilibration with the iron surface. All correlation coefficients for the linear, first-order fit used for the calculation of rate constants exceeded 0.99. For convenience, rate constants are presented in terms of per h/g Fe and in terms of L/h/m². Since the application of iron in a permeable treatment wall is based on mass of iron used in the installation, all discussion of rate constants in this paper use rate constants in terms of per h/g Fe.

For both the 100-mesh iron and the coarse iron filings, treatment and sonication influenced specific surface area. Regardless of the initial unwashed specific surface area of the unsonicated sample, washing in 5% sulfuric acid increased specific surface area for the two iron types an average of 1.17 m²/g. Increases in surface area post-sonication varied somewhat by iron type and treatment, but averaged 1.11 m²/g.

Considering acid-washed samples, sonication increased surface area 1.12 and 0.99 m²/g in the 100-mesh iron and iron filings, respectively. The changes in the surface areas reflect a cleaner, more open surface area but also could be related to, in some cases, the breakdown of the particle itself into smaller pieces with greater surface area to bulk ratio. Sonicated unwashed samples of these irons produced specific surface areas within an average of 6% of those measured for their unsonicated, acid-washed counterparts.

Acid-washed iron was more effective in the removal of TCE for both types of iron. One hundred-mesh iron was shown to be more reactive than iron filings under the same conditions. This is due to the increased surface area for 100-mesh iron or acid-washed iron and agrees with the findings of previous researchers that the reaction is surface area dependent [6,22].

Data obtained from XPS analysis (summarized in Table 3) show that washing iron with 5% sulfuric acid reduces the C–H/C¼O ratio indicating a decrease in surface oxides accompanied by an increase in the formation of highly reactive (nonstoichiometric) oxides due to the exposure of fresh reactive surface. The nonstoichiometric oxide layer indicates activation of the iron surface. Activation of the metal surface, actually
the initiation of corrosion, is a basic step in organometallic chemistry [24]. The energy associated with Fe(2p)3/2 (FWHM-Fe) in the acid-washed iron is the lowest of all the samples indicating a very reactive surface. The valence band scan (0–20eV) of this sample exhibited a broad band from 2 to 8eV which is characteristic of highly reactive, nonstoichiometric iron oxides and is indicative of hybridization in the electron density of states between O(2p) and localized Fe(3d) band.

Vacancy formation in the oxide lattice structure in the subsurface leads to defects in the oxide lattice and creates a flow-path for interaction of ionic species with the iron. Sonication has been shown to create lattice defects in lithium [15], zinc [16], and copper catalysts [17].

Ultrasound application improved rate constants for TCE disappearance with unwashed iron filings by 24.1%. Since the thicker oxides and corrosion products inhibit dehalogenation, the cleaner surface resulting from ultrasound application provides more opportunity for electron transfer reactions to occur [25]. XPS data show that carbonyl oxygen (C=O) is increased after application of ultrasound to unwashed iron. The presence of multiple elemental species causes broadening of the carbon C(1s) peak. This conclusion is supported by the decrease in the C–H/C in carbonyl (C=O) ratio. The surface atomic concentration ratio of total iron to oxygen (Fe/O in Table 3) decreased and the simultaneous broadening of the oxygen O(1s) peak (FWHM-O) indicate that oxides increase as the C–H/C in carbonyl (C=O) ratio decreases. Sonication broadens the natural line width of the Fe(2p3/2) iron peak (FWHM-Fe). When considered with associated rate constants for unwashed iron, this implies that sonication removes chemically less reactive material and exposes a more reactive underlying surface.

Unwashed, unsonicated iron samples exhibit sharper peaks for iron, which is indicative of less active material. Unsonicated material shows less oxide formation, mostly weakly adsorbed oxygen molecules, because of the localization of the Fe(3d) density of states. Sonicated filings exhibit a broad iron peak and, therefore, should yield much greater reactivity for dechlorination. The typical broad valence band of iron oxides is due to the hybridization of Fe(3d) and O(2p) density of states.

### 3.4. Oxidized iron: sorption or reactivity

The high rate constants for oxidized irons relative to their acid-washed counterparts seemed unreasonable, considering that the oxidized surface should be passivated. Scherer et al. [1] summarized three possible modes of reduction reactions at the interface between solid (oxide or metal/oxide) and the solution phase: localized defects, resonance tunneling or complexation. Since the oxidized iron may feature areas where any of these three mechanisms could occur, it was expected that some degradation products would be observed. However, the oxide layer on intentionally oxidized iron was relatively thick yielding a surface with many layers of overlapping oxide, far greater than the approximately 10 Å thickness suggested as a limit for direct tunneling of electrons [1].

Acid-washed filings generated degradation product concentrations as high as 9 mg/L while oxidized filings generally yielded stable concentrations of no more than 1 mg/L. The first-order rate constant for the disappearance of TCE with oxidized filings was 46.8% higher than its counterpart for acid-washed filings. Since the concentration of by-products was much lower for the oxidized iron system, it was hypothesized that TCE disappearance reflects sorption with little accompanying degradation to less chlorinated by-products.

The role of sorption to unreactive sites is not entirely understood. Burris et al. [26] performed experiments to determine the population and effects of nonreactive sites on the iron surface. His work suggested that most of the iron surface consists of unreactive sites and that it is unclear what happens to the TCE that sorbs to them. This article infers that the rates of sorption of individual compounds can be used to adjust degradation rate

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unwashed</th>
<th>Acid-washed</th>
<th>Groundwater-soaked</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>No US</td>
<td>US</td>
<td>No US</td>
</tr>
<tr>
<td>First-order rate constant, kobs (per h/g Fe (×10⁻³))</td>
<td>2.70</td>
<td>3.36</td>
<td>4.74</td>
</tr>
<tr>
<td>FWHM-Fe (±0.1 eV)</td>
<td>4.5</td>
<td>4.7</td>
<td>4.0</td>
</tr>
<tr>
<td>FWHM-C (±0.1 eV)</td>
<td>1.9</td>
<td>2.3</td>
<td>2.0</td>
</tr>
<tr>
<td>FWHM-O (±0.1 eV)</td>
<td>4.0</td>
<td>4.5</td>
<td>4.2</td>
</tr>
<tr>
<td>Fe/O</td>
<td>0.351</td>
<td>0.244</td>
<td>0.252</td>
</tr>
<tr>
<td>C–H/C in C=O</td>
<td>2.42</td>
<td>2.88</td>
<td>2.84</td>
</tr>
<tr>
<td></td>
<td>4.62</td>
<td>3.93</td>
<td>3.99</td>
</tr>
</tbody>
</table>

aN/A, not available.
constants to a more accurate representation of the chemical reactions taking place at the surface.

3.5. Nonchlorinated fraction of products

Due to the capability of ultrasound to activate catalyst surfaces [15–17] and the observed increases in rate constants for most iron samples, the question arose whether sonication changes the degradation process or simply increases the rate. To learn more about these possible processes, the nonchlorinated fraction of two-carbon degradation products (expressed as mole fraction) were plotted against half-life reductions in TCE (Figs. 2a–c). In the case of acid-washed iron, the rate of TCE disappearance remained almost constant regardless of sonication history but the percentage of nonchlorinated by-products increased from 5–7%. A more striking contrast was observed for unwashed filings where the nonchlorinated by-product fraction increased by about 10% (Fig. 2c). The divergence in two-carbon product composition due to sonication was noted as early as one half-life of TCE loss.

If sonication were only creating more active sites, then the rate of TCE disappearance would have increased with no effect on the speciation of the by-products. The increase in the fraction of nonchlorinated by-products can be at least partially attributed to a change in the interaction between TCE (or its by-products) and the active sites on the solid surface. It is theorized that TCE molecules come into contact and are more strongly sorbed to ultrasound generated active sites than the sites available on iron not exposed to ultrasound, and therefore continue through the mechanism (mechanistic pathway suggested by [27] to complete dechlorination.

If the above hypothesis is true and active sites are held by single molecules through complete dechlorination (with prior ultrasound treatment) then fewer TCE molecules would come in contact with active sites per unit of time. Therefore, these data suggest an increase in both number of active sites and increased affinity to the chlorinated solvent and chlorinated by-products.

3.6. Scanning electron micrographs

In order to determine if ultrasound would be effective when used on material corroded by chlorinated solvents, the groundwater environment, or simple oxidation from air, iron was exposed to various conditions and then treated with ultrasound (SEMs shown in Figs. 3a–h).

Acid-washed, 100-mesh iron was aged for 1 month in 200-mg/L TCE solution, then removed and dried under nitrogen gas. A sample treated with ultrasound for 120 min and a sample that had received no ultrasound treatment were examined using SEM. Figs. 3a and b show the aged sample and the aged, ultrasound treated sample, respectively. Unwashed iron filings that have been soaked in natural groundwater for several months are shown in Figs. 3c and d before and after exposure to ultrasound. Intentionally, oxidized 100-mesh iron and iron filings (both before and after ultrasound) are shown in Figs. 3e–h.

In all instances, the unsonicated samples (Figs. 3a, c, e, and g) showed significant coverage of corrosion products over most of the surface area; however, the respective sonicated samples were visibly cleaner (Figs. 3b, d, f, and h), with a reduction in material size and coverage. The SEMs shown illustrate the effects that natural groundwater, high concentration of a chlorinated solvent, or oxygen exposure can have on iron in the subsurface. After exposure to ultrasound (Figs. 3f and h), some fine cracking of the oxide surface is
The cracks in the surface present a new pathway for electron transfer through diffusion of the aqueous solution to the Fe⁰ surface as well as more Fe²⁺ diffusion from the bottom of the pit [28]. Since the data shown suggest that iron with an obstructed surface area will have lower degradation rate constants, a technology such as ultrasound that can clean the surface in situ is a necessary component of treatment walls under certain groundwater conditions.

4. Conclusions

The reaction of TCE with iron has been shown to be surface area dependent. As corrosion products and precipitates build up on the surface, the reaction with TCE is diminished because the unoccupied iron surface area is decreased. Ultrasound has been demonstrated to remove corrosion products, precipitates and other debris from the iron surface. This serves to increase the active iron surface, improve reaction rates and, increase the concentration of terminal by-products. The application of ultrasonic energy is a direct approach that cleans the iron surface and restores reactivity.

Both 100-mesh iron and iron filings, under a variety of conditions, were positively impacted by the application of ultrasound. SEMs illustrate the corrosion that occurred when iron had been exposed to TCE (aqueous) or natural groundwater for extended periods of time. Brief exposures to oxygen obviously degrade the iron surface quickly. However, treatment with ultrasound removed precipitates and debris to leave the surface in near acid-washed condition. Although heavily occluded surfaces may sorb TCE, data verify that clean surfaces actually are more reactive and produce more terminal by-products.

Considering that the goal of this technology is to completely dechlorinate the parent compound, the data showing an increased fraction of nonchlorinated by-products represent an important benefit of ultrasound treatment. The use of ultrasound can decrease the time necessary to convert the parent compound to fully dechlorinated end products.

XPS analysis of iron samples provided important surface chemistry information. It is clear that iron
treatment and sonication history change both the relative presence and the bonding nature of an element on the iron surface. These changes are reflected, in turn, in changes observed for first-order rate constants for TCE degradation.

As contaminated groundwater flows through the treatment wall, 100% destruction is desired. Since the wall is limited in thickness, a fast reaction rate ensures maximum conversion to harmless species. The reaction rate will be rapid initially since passivation has not occurred. However, corrosion of the iron surface will eventually serve to decrease the reaction rate and result in effluent concentrations that could exceed regulatory limits. Inserting ultrasound probes into the treatment wall and periodically applying ultrasonic energy would “rejuvenate” the wall resulting in a sustained reaction rate.

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References


