Chapter

Dissolvable Magnesium Alloys in Oil and Gas Industry

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Abstract

Invented and continuously optimized during two decades of the shale revolution that completely transformed the global energy market, dissolvable magnesium (DM) alloy technology has advanced significantly in both performance improvement and cost reduction, and thousands of tons of Mg alloy are consumed annually by oil and gas industry to fabricate downhole tools, including dissolvable hydraulic frac plugs. In this book chapter, every aspect of this technology will be reviewed, including history, development routes, manufacturing process, dissolving mechanism and control, failure analysis and prevention, influence of environments, delayed coating, field experience, etc., and outlook will be provided at the end for future development.

Keywords: dissolvable magnesium, temporary coating, frac plug, hydraulic fracturing, high-temperature magnesium alloy

1. Introduction

The world's first oil well was drilled in Titusville, Pennsylvania by Edwin Drake in 1859, producing a mere 40 barrels a day [1]. Drake's success inspired the continued exploration of oil in the United States as well as globally. A period from the 1930s to the 1960s led to the discovery of many of the world's largest oilfields. However, from 2000 to 2022, no discovered oilfield has exceeded the proven reserves of any existing top 20 giant conventional oilfields [2]. The International Energy Agency (IEA) shows all conventional global oil production plateaued around 2005. Despite the global decline from conventional oilfields, global supply has increased and actually outstripped increased demand in the past 20 years [3].

Aside from advancements in enhanced oil recovery (EOR) methods increasing production, unconventional resources became a major source of global oil supply in the past two decades. Previously disregarded unconventional shale oilfields with permeabilities magnitudes less than conventional oilfields became economical by hydraulically fracturing horizontal wells [4]. Drilling through oil-bearing shale layers increases the reservoir exposure to the wellbore. Hydraulic fracturing involves an array of reciprocating positive displacement pumps over-pressuring the reservoir in the vicinity of the wellbore to create new fractures or open existing ones. Sand is pumped into the resultant fractures to create high permeability pathways in shale. Shale has permeabilities orders of magnitude less than conventional formations [5].

Permeability is a controlling factor on how much fluid may be produced from the reservoir; a higher permeability leads to higher production. The fracturing operation is repeated along the wellbore in targeted zones, increasing the overall production of the well, thus creating economically viable wells from previously marginal formations. During fracturing, zones are isolated from one another by a plug, which is conveyed downhole and allows the over-pressuring [6].

The first plugs were made of cast iron that needed coiled tubing to drill through after fracturing to reestablish communication downhole and start production at the wellhead. Composite plugs supplanted cast iron plugs as composite mills quicker than iron [7]. A major advancement was made during the past decade in the creation of dissolvable frac plugs, which react in situ, thus eliminating the need for coiled tubing. Eliminating coiled tubing also allows for zonally isolating longer horizontal sections that would otherwise be impossible to mill [8]. This technology has reshaped the market landscape of shale oil/gas development, and its success is the result of invention of advanced dissolvable magnesium alloy (**Figure 1**).

Development and application of dissolvable Mg alloy is a relatively new technology in oil and gas business. It was invented by US service companies and optimized worldwide by research institutions and alloy companies to improve property and reduce cost. The first mainstream application reported is a dissolvable ball, developed by Baker Hughes in 2010 to activate downhole equipment [9]. Before that, this ball must be milled out or flow back to start well production, and the application of this self-disappearing technology saves operators significant amount of lead time and thus operation cost. In the early stage, expensive powder metallurgy (PM) method is used to form the perfect galvanic cell structure. In a typical manufacturing process, high chemical potential metals, such as Ni, Fe, etc., are coated on the Mg alloy powder surface and then sintered together through an industrial hot isostatic pressing (HIP) process. Since Mg alloys are soft, certain enhancement phases are added to improve mechanical strength. As shown in **Figure 2**, Mg and Ni alloy phase form nearly perfect galvanic cell structures. Its physical properties and dissolving speed can be systematically tuned. This technology achieved significant commercial success, and lots of

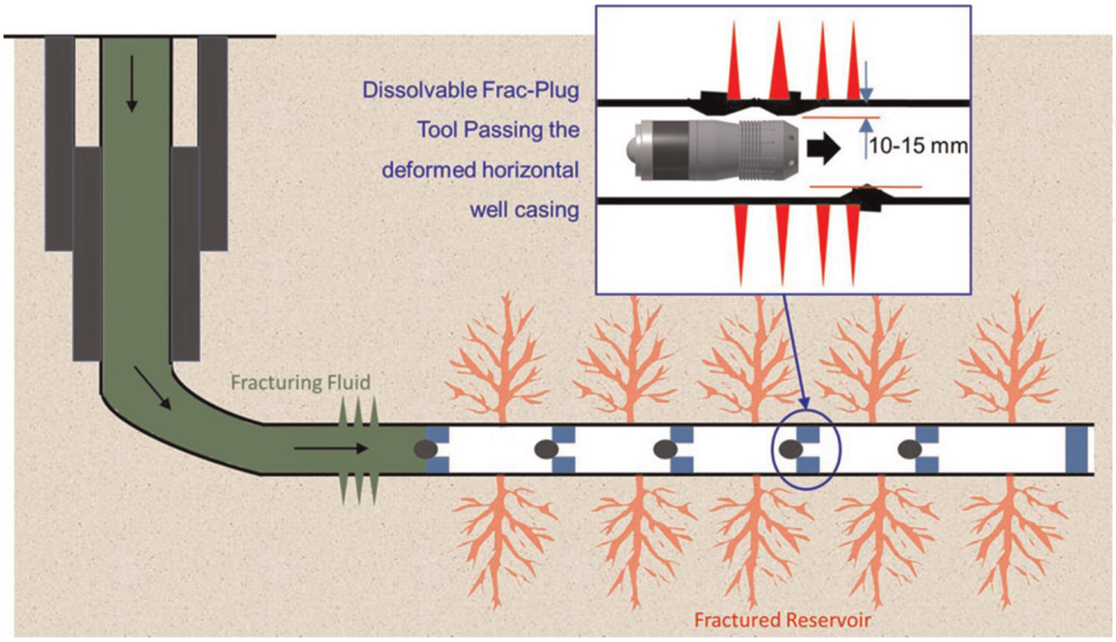


Figure 1.
Schematic of a hydraulically fractured horizontal well [9].

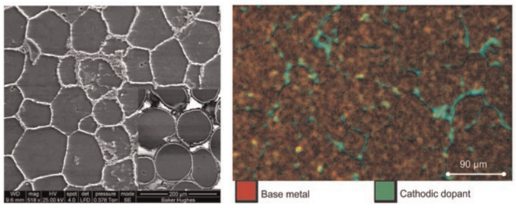


Figure 2.
SEM micrograph of DM material made by powder metallurgy method (left image, [10]). The inset shows a cross-section view of as coated matrix powders before compaction. SEM-EDS image of DM alloy developed by Halliburton (right image, [11]).

companies followed with their own formulations and process method. Given its success, this method still suffers from following issues:

1. High cost: This technology requires atomization of Mg alloys, advanced coating method, and HIP process, all of which are not cost-efficient for oil and gas business where product is a commodity.

2. Low ductility: DM made from PM method usually have low elongation (typically <3%), which is not an issue for ball shape product that does not requires plastic deformation but is not applicable for other parts of plug that requires much higher ductility (**Figure 3**).

With the frame of powder metallurgy, another low-cost processing method was used to reduce the cost. For example, powder mixing method is used to replace chemical vapor deposition (CVD) coating, cold compaction followed by hot extrusion is used to replace expensive HIP process, etc. Product price of DM alloy quickly drops thanks to the consolidation and severe competition between oil and gas service providers. However, these alloys can still not be used by other mechanical parts that require reasonable amount of ductility until a cheap casting method was introduced into market by Halliburton. Their work shows that DM alloy can be made by traditional direct casting and post-heat treatment. The galvanic cell is formed by controlled phase segregation of high chemical potential metals at Mg alloy grain boundaries (**Figure 2**). Therefore, atomized metal powder is no longer needed, and cost of DM alloy is close to other commercial-grade Mg alloys. Most importantly, reasonable ductility is finalized and achieved, and all dissolvable plugs (**Figure 4**) are introduced by various oil and gas providers including Baker Hughes, Halliburton, NOV, etc.

Like most commercial Mg alloys, DM alloy also suffers from strength loss when temperature is above 120°C and cannot be used for high-temperature wells that could reach 220°C. Therefore, various kinds of a rare-earth elements were further

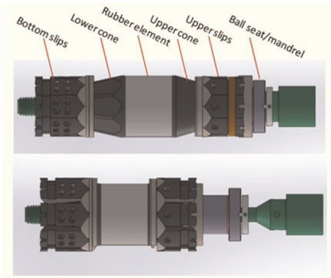
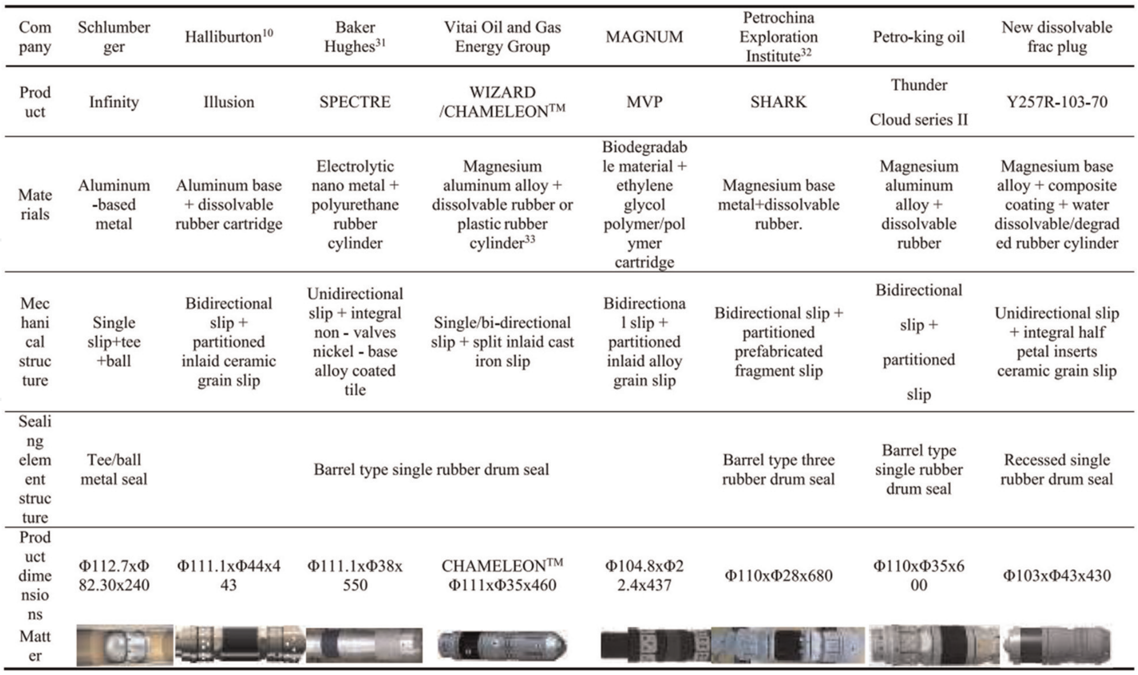


Figure 3.
Labeled plug before actuation (top) and actuated (bottom).



Company	Schlumberger	Halliburton[10]	Baker Hughes[31]	Vitai Oil and Gas Energy Group	MAGNUM	Petrochina Exploration Institute[32]	Petro-king oil	New dissolvable frac plug
Product	Infinity	Illusion	SPECTRE	WIZARD /CHAMELEON™	MVP	SHARK	Thunder Cloud series II	Y257R-103-70
Materials	Aluminum-based metal	Aluminum base + dissolvable rubber cartridge	Electrolytic nano metal + polyurethane rubber cylinder	Magnesium aluminum alloy + dissolvable rubber or plastic rubber cylinder[33]	Biodegradable material + ethylene glycol polymer/polymer cartridge	Magnesium base metal+dissolvable rubber.	Magnesium aluminum alloy + dissolvable rubber	Magnesium base alloy + composite coating + water dissolvable/degraded rubber cylinder
Mechanical structure	Single slip+tee +ball	Bidirectional slip + partitioned inlaid ceramic grain slip	Unidirectional slip + integral non - valves nickel - base alloy coated tile	Single/bi-directional slip + split inlaid cast iron slip	Bidirectional slip + partitioned inlaid alloy grain slip	Bidirectional slip + partitioned prefabricated fragment slip	Bidirectional slip + partitioned slip	Unidirectional slip + integral half petal inserts ceramic grain slip
Sealing element structure	Tee/ball metal seal	Barrel type single rubber drum seal				Barrel type three rubber drum seal	Barrel type single rubber drum seal	Recessed single rubber drum seal
Product dimensions	Φ112.7xΦ82.30x240	Φ111.1xΦ44x443	Φ111.1xΦ38x550	CHAMELEON™ Φ111xΦ35x460	Φ104.8xΦ22.4x437	Φ110xΦ28x680	Φ110xΦ35x600	Φ103xΦ43x430
Matter								

Figure 4.
Comparison of characteristics of similar dissolvable frac plugs [12].

introduced from thermally stable precipitates. Certain rare metals have been found to increase elongation of DM alloy to almost 30%, making metal-to-metal seal application possible. To answer oil price downturn from since, manufacturing of DM alloy started to move to China, where rare-earth resource is abundant and Mg production is dominated. DM alloy is no longer an expensive high-end material but a commodity accessible for all oil and gas service providers around the world to develop various kinds of applications besides hydraulic fracturing plugs.

2. Dissolvable magnesium design, processing, and mechanism

2.1 Dissolvable frac plug

Dissolvable plugs are composed of one or more materials that react when in the wellbore. The current generation of polymers used in plugs, mostly polyglycolic acid (PGA), are limited from 80 to 130°C. Magnesium is the typical choice for metallic plug components in windows of 40 to 175°C. Operators generally require plug functionality for eight hours, with complete dissolution occurring within 15 days [12]. The general operating principles of a frac plug are to convey it from the surface to the targeted zone, actuate it to set in the casing, and achieve a tight seal that is to be held for one to 24 hours, after which it is left to dissolve so that production may start. Pressure is built by conveying a ball down to the plug, where it will seat, blocking the inner diameter that is the final possible path of communication between the surface and the area below the plug.

Generally, a plug will have an angled recess at the top of the plug, which operates as the ball seat. Many designs integrate the ball seat into the mandrel, a hollow tube that the other components are assembled on. The setting tool is connected to the plug through this component. The setting tool supplies the force that pushes the parts together on the mandrel, increasing the plug diameter due to a ramp design that forces the slips and elements into contact with the casing (**Figure 3**). The slips have small hard teeth that penetrate the casing, anchoring the plug to the casing. Petal designs of slips can come in an upper and lower pair. Other designs may utilize a barrel slip design. The element is typically made of dissolvable rubber, although some plugs utilize a metal-to-metal seal design (**Figure 3**). The element seals the outer diameter between the casing and the plug. A bottom cap is used to secure all components on the assembly during deployment.

Requirements for the plug material vary widely depending on the operator, design, temperature, fluid, and individual component requirements. At a given temperature on a plug, one component may require high ductility whereas another requires high strength. The same plug design functioning at 95°C may be inadequate at 175°C due to deteriorated mechanical properties or accelerated corrosion of the base alloy. Materials with a wide array of properties must be available to match the varying wellbore conditions. The rate of development for new formulations can be outstripped by delivery dates for product. That is why each oil service providers have their own material grades or plug designs to meet requirements of specific well conditions or markets (**Figure 4**).

2.2 Dissolution mechanism and dissolving dynamics

2.2.1 Galvanic cell structure

Dissolvable magnesium alloys rely on intercellular galvanic corrosion induced by noble impurities in chloride-bearing wellbore fluids. The dissolution rate is controlled by the type and fraction of secondary phases in the matrix. Beyond determining mechanical properties, the secondary phases are more cathodic than the magnesium matrix, causing hydrogen gas and magnesium ions to form as a byproduct of the reaction [13]. The reaction proceeds as follows, typically in a brine solution:

$$\mathrm{Mg} + 2\mathrm{H_2O} \rightarrow \mathrm{Mg(OH)_2} + \mathrm{H_2}\ (\mathrm{gas}) + \mathrm{heat} \qquad (1)$$

Figure 5 shows galvanic series of various metals and alloys, which determines their nobility. When two metals are submerged in an electrolyte, while also electrically connected by some external conductor, the less noble (base) will experience galvanic corrosion. Magnesium is the least noble structural metal and can form a galvanic cell with almost any of the metals/alloys in the series. Therefore, it is possible to mix it with noble metals to form dissolvable alloys based on galvanic corrosion. It is reported that Fe powder [15] or Ni powder [16] can be mixed during melting and casting process to make dissolvable alloys for oil and gas industry. Also, a powder-metallurgy-like structure including a relatively reactive metal or alloy can be combined with other compositions to develop galvanic couples [17]. Additions of copper and/or nickel to magnesium will create a meaningful accelerated corrosion rate that may be tuned to the application temperature and salinity. For example, a composition can include an alloy of magnesium or aluminum that is combined with one or more of Cu, Fe, and Ni, among a few transition-metal elements to develop galvanic couples. Copper and nickel form high electropotential intermetallic compounds along the grain boundaries of the magnesium matrix phase. These noble intermetallic act as an archipelago of cathodes, accelerating the corrosion of the magnesium alloy.

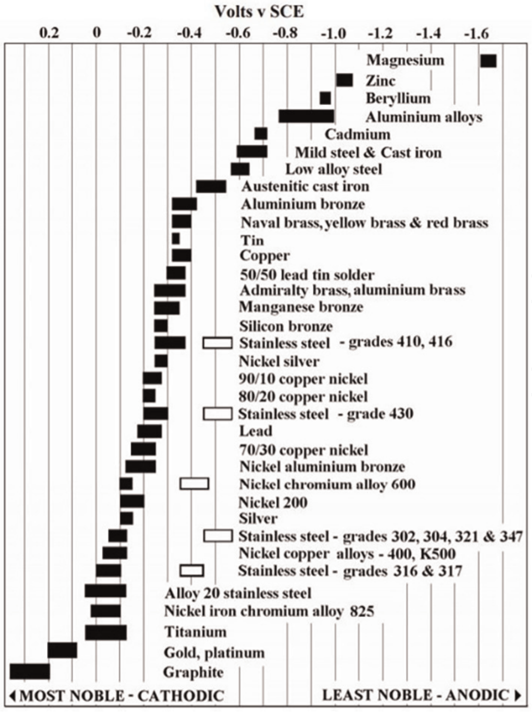


Figure 5.
Galvanic series (or electropotential series) of metals and alloys [14].

2.2.2 Environmental dynamics: influence of temperature, salinity, and dissolved gas

The reaction kinetics of the dissolution mechanism of magnesium has a clear dependence on temperature and salinity. Taking one of our dissolvable magnesium alloy grades AZ31–1, for example, for the reaction to proceed, some chloride must be present, as evidenced in **Figure 6**. Tap water has a very small amount of chloride that allows the reaction to proceed, albeit at a slow rate. Increasing the chloride concentration leads to a nonlinear increase in the dissolution rate. For a given chloride

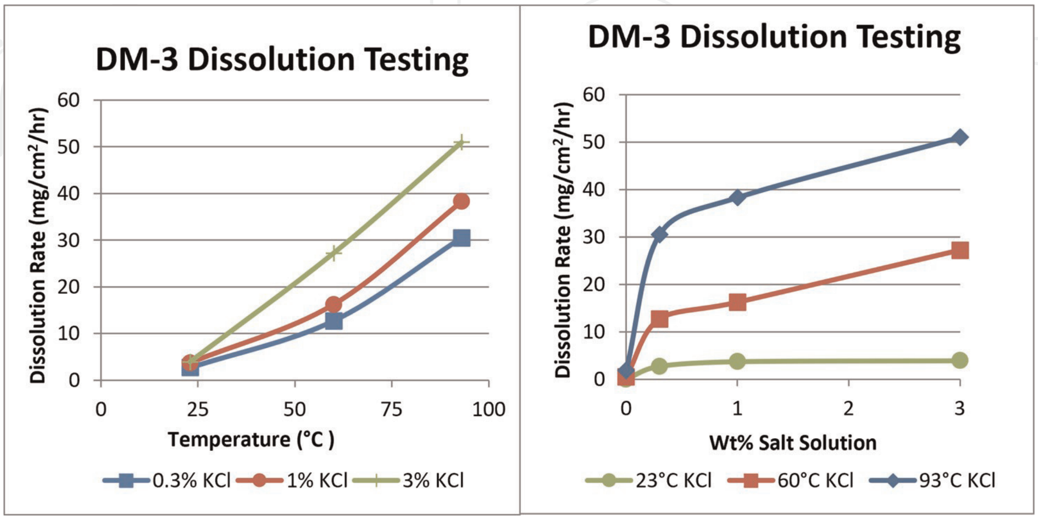


Figure 6.
Dissolution of alloy AZ31–1 in tap water, 0.3 wt% KCl, 1 wt% KCl, and 3 wt% KCl at 23°C, 60°C, and 93°C, respectively. The chart on the left shows the dissolution rate as a function of salinity. The righthand chart demonstrates the dissolution rate as a function of temperature. Measurements performed by CNPC USA.

concentration, the reaction rate is close to linear with increasing temperature. Due to the increasing rate, material is developed for different temperature applications, or specialized coating is applied to ensure sufficient operational life.

Besides salinity and temperature of fluids, dissolved gas also plays a key role but is often ignored by application engineers. Estimates on how quickly a plug will dissolve in the lab are often much shorter than what is measured in the field. After years of studying the dissolution rate in the traditional water bath method, that is measuring weight loss after soaking in water bath for a certain period of time, a comparison was made for testing an alloy in several ways while maintaining a temperature of 95°C and a salinity of 1 wt% KCl. The water bath test dissolution rate fell within the range of the unpurged autoclave, pressurized or not. There was a substantial decrease in the dissolution rate of the autoclave where the nitrogen was used for purging entrapped air. The delayed dissolution rate of the material in the purged autoclave appears to be more representative of the deoxygenated downhole environment. If a plug takes 50% longer than estimated to dissolve based on calculations made from water bath testing, every stage of every well that uses dissolving magnesium is taking longer to come online, thus reducing time to full production.

2.3 Dissolvable magnesium alloy design

Each well is unique in certain ways, for example temperature, pressure, fluid conditions, operational procedures, etc., and the dissolvable plug is also an assembly of various complex parts that bear different stress and strain during application. Therefore, one grade of DM cannot fit for all **DMs**, that is, a great variety of DMs must be developed with different dissolving rates to satisfy well conditions, as well as mechanical properties to meet requirements of plug design. Balanced by application requirements and supply chain, DM is usually categorized first by temperature (low-temperature grade, medium temperature grade, high-temperature grade), by corrosion rate (low rate, general rate, fast rate), by strength (low yield, general, high yield), or by ductility (general and high elongation).

As discussed in introduction, DM technology is developed by an oil service company in the US, and they keep the cost and production scale in mind even at the beginning because of low price of the final product. Since core technology of DM is to form galvanic cell microstructure, the most natural way to achieve industrial goal is to modify the formulation of mature Mg alloy grades through micro alloying. Different from other dissolvable alloy technology developed by academic community like those used in bio or medical field, detail formulation of each commercial DM grade typically kept confidential, but the technical route is similar and open to public. In this section, the general technique routes are illustrated on how magnesium can be alloyed with many elements to enhance properties such as strength, castability, workability, and corrosion rate.

2.3.1 Alloying for mechanical properties

For the traditional Mg alloy grades, aluminum is commonly added to magnesium alloys to form the β phase ($Mg_{17}Al_{12}$) above two weight percent, increasing the strength at the expense of ductility. Alloying with zinc increases both strength and ductility [18], leading to many alloys such as ZK60 being developed as a high-strength low-cost commercial alloy. The addition of zirconium acts as a grain refiner through heterogeneous nucleation in the melt, resulting in further increases in mechanical properties. However, zirconium will react in situ with aluminum so that the two cannot be used together. Various rare earth elements (neodymium, cerium, gadolinium, yttrium, etc.) are added to create high-strength, thermally stable alloys such as WE43. Rare earth added to aluminum-alloyed magnesium has a positive effect on mechanical properties [19]. Others have reported the addition of sufficient rare earth creates a long-period stacking ordered (LPSO) structure that significantly increases the mechanical properties and thermal stability of an alloy [20]. For commercial DM in oil and gas industry, this microalloying technology or microstructure is still utilized in the exact same way. The only difference is to add suitable noble impurities at reasonable content to make conventional magnesium alloy "dissolvable" without interfering with microstructures that give alloy its mechanical properties.

2.3.2 Alloying for dissolution rate

After an existing commercial alloy or internally developed magnesium formulation has been selected, elements promoting the galvanic cell effect are selected. In one instance, one or more alloying elements are added to create a galvanically-active intermetallic particle. These are created during the casting phase where bulk magnesium alloy melt temperature is less than the temperature of the introduced alloying elements. Solid particles of any unalloyed elements are cooled**,** and an ***in situ*** precipitate of any solid particle forms. While avoided in typical applications due to the decrease in corrosion resistance, these intermetallic particles are intentionally created to accelerate the dissolution of the resulting alloy. The type and amount of alloying elements added are modified to obtain the desired corrosion rate in the magnesium alloy.

Another method of creating a dissolvable magnesium alloy is to select elements that prevent the naturally occurring passive MgO surface layer from reforming in a corrosive media. Mercury and gallium both possess this ability and have a high solubility within a magnesium matrix. Above the eutectic point, these elements and their precipitates will form along the grain boundaries, creating areas with vast electropotential differences.

The most common method of appreciably accelerating the corrosion rate of a magnesium alloy is the addition of copper, nickel, and tin. An addition of <4 weight percent copper or < 1 weight percent nickel is adequate to create secondary cathodic phases that accelerate corrosion of the alloy.

2.3.3 Cast magnesium alloy base

Traditionally, cast Mg alloys often contain Al, Mn, Zn, Ag, or rare-earth (RE) elements as one of the major alloying additions. Aluminum is the major alloying element for common casting alloys made in sand, permanent mold, and high-pressure die casting. High-integrity castings for aerospace applications are made with other casting alloys based on Ag, Zn, and Y rather than Al [21]. Very few manufacturers utilize cast method to make magnesium dissolvable component because the casted product cannot achieve mechanical strength required by applications. However, high-quality casting is the first step to make high-quality wrought products. During our development, several groups of elements are found essential during casting step.

The first group of low-melting-point alloying elements (Li, Bi, Ga, In, Pb, and Sn) reduces the liquidus temperatures of the binary alloys, which is generally good for castability of the binary alloys. Alloying with these elements increases the dissolvability of the alloys. The second group of alloying elements (Ca, Si, and Zn) forms various intermetallic phases, which often provide strengthening to the alloys. Zirconium is an effective grain-refiner for aluminum-free magnesium alloys due to a peritectic reaction in Mg-Zr system. Cerium is also a good grain refiner and can randomize the texture of wrought magnesium alloys while increasing the corrosion resistance. Iron does not form any intermetallic phases within the matrix. Iron is considered as impurity element because it causes micro-galvanic corrosion in Mg alloys. When iron content is high, Mg-Fe-based alloys become dissolvable. It has been reported that degradable alloys can include Mg-Li alloys enriched with tin, bismuth, or other low-solubility alloying elements [22].

2.3.4 Wrought magnesium alloy base

Of commercial extrusion alloys, AZ31 is most widely used in nonautomotive applications. With higher aluminum contents, AZ61 and AZ80 offer higher strength than AZ31 alloy, but at much lower extrudability. The high-strength Zr-containing ZK60 was designed for applications in racing cars and bicycles, such as wheels and stems. WE43 and WE54 have exceptional high-temperature strength and creep performance and can be used up to 260°C. These alloys form the baseline compositions for many compositions of dissolvable magnesium alloys. To take full advantage of well-established manufacturing facilities of these commercial grades, most DM alloy grades are modified from these matures traditional grades for cost reduction or short development time. For example, AZ31 is the basic system to develop general DM grades, AZ61 or ZK 60 are the base for high-strength DM grades, and WE series are typically referenced to make high-temperature DM grades.

Cold working, solutionizing, and heat treatment all have an influence on not just the mechanical properties, but the resulting dissolution rates. The precipitation of phases of varying electropotential may be accomplished through thermomechanical processing. For a given chemistry, grain refinement will create a multiplicity of smaller cells that on the net have more surface area. As corrosion occurs, grains detach from the bulk of the material. Smaller grains detaching due to corrosion result in less mass loss per unit volume than one large grain, thus leading to a measurably smaller corrosion rate.

2.4 Dissolvable magnesium alloy processing

Due to cylindrical shape of final products (**Figures 2** and **3**) and high strength requirements, casting and subsequent extrusion into bar or tubular shape has been finalized by industrialists as the most cost-efficient route to manufacture dissolvable Mg alloy raw material on large scale after over a decade of technology iteration, as discussed in the introduction. High-quality melting and casting could significantly reduce the content of impurities and defects, while hot extrusion and related heat treatment in well-controlled processes are essential to achieve desired microstructures and mechanical properties. All these two steps will be illustrated in this section.

Melting and casting of dissolvable magnesium alloys are the same as non-dissolvable alloys. Many manufacturers utilize the same equipment to create both types of alloys. Of note is the preference for direct chill (DC) semicontinuous casting alloys (**Figure 7**). Molten metal is poured into the open mold from the top. As the partially solidified billet/slab emerges from the mold, water impinges directly on the casting surface. Steady-state casting conditions are achieved when the sump profile ceases to evolve with time relative to the mold. The casting process stops when the desired cast length is obtained or the bottom of the pit is reached. For magnesium alloys, billets up to 500 mm in diameter and 2000 mm in height are produced. The

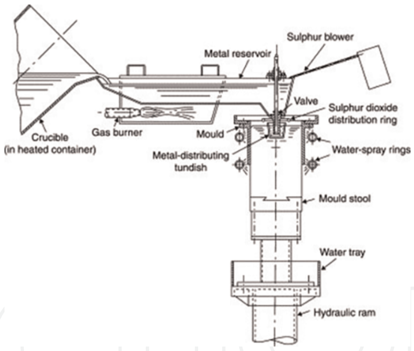


Figure 7.
Schematic of the DC cast process for magnesium alloys, indicating the different heat-transfer regimes [23]. Figure reproduced with permission from Elsevier.

advantages of DC products are high cooling rates due to water spray and no visible cracks as compared to castings in a mold. Also, the DC casting method reduces the internal stress in the cooled material by allowing contractions on all sides, as opposed to only on the top of the ingot in a traditional trough mold [23].

Experientially, of the various methods for shaping magnesium, direct chill casting is the preferred route. In our work, three DM alloy grades, AZ91–1, MS-RE-1 (medium strength rare earth), and HD-RE-1 (high ductility rare earth), were cast by two different methods, vacuum induction melting (VIM) and direct chill (DC) casting, and extruded by the same 6:1 reduction ratio. Sampling tensile from the quarter radius longitudinal direction allowed for a comparison between the two materials. In all but one instance (HD-RE-1 UTS), the mechanical properties of the DC cast material are superior to the VIM cast equivalents (**Figure 8**). The dissolution rate is also found to decrease for each alloy manufactured by DC cast (**Figure 9**). The increased

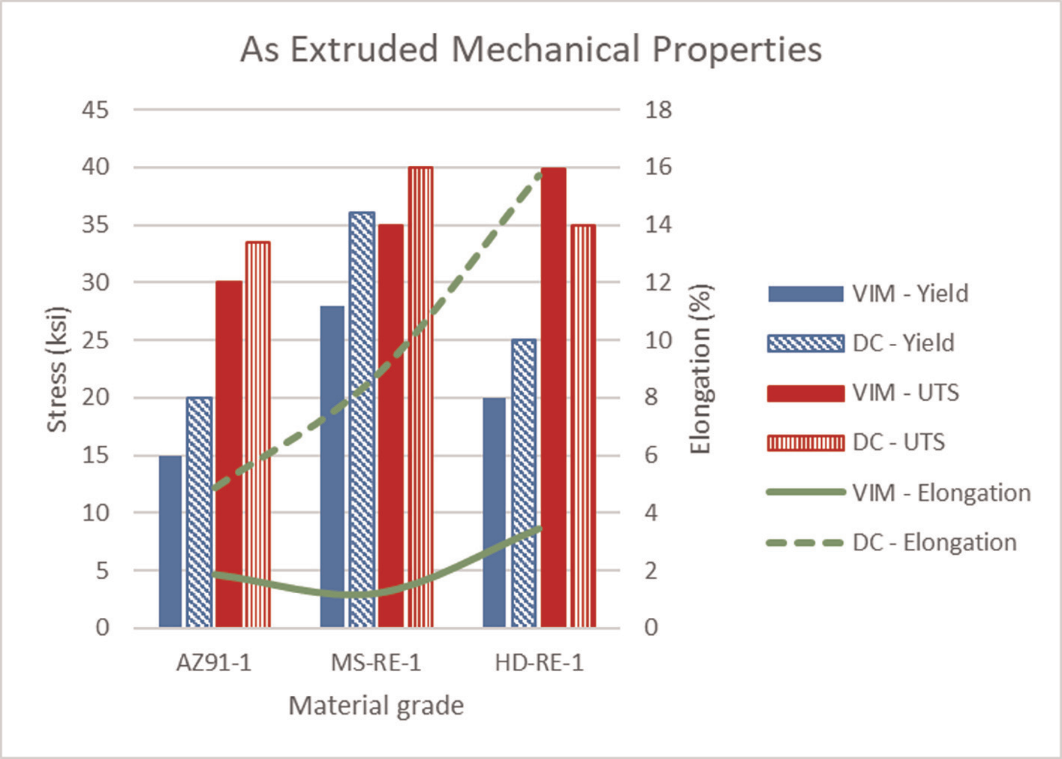


Figure 8.
Comparison of the as-extruded mechanical properties from two casting techniques: VIM and DC.

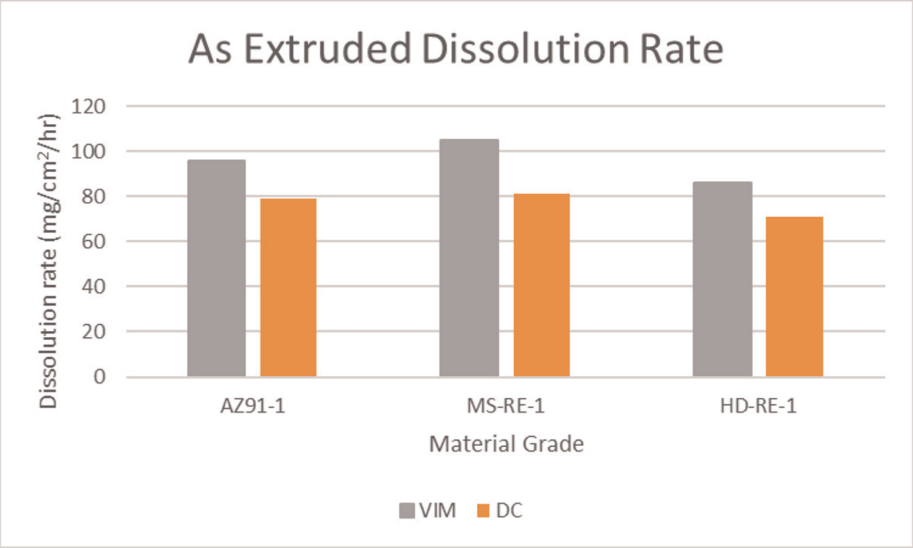


Figure 9.
Comparison of the dissolution rate of material cast by VIM and DC.

mechanical properties and decreased dissolution rate indicate a finer grain structure of DC castings. The melt agitation and fast cooling from DC casting make it the first technical choice for producing dissolvable magnesium alloys.

Casted billet is typically full of defects and does not exhibit enough strength or elongation required by dissolvable plug application. To meet these high requirements, the next step is to hot extrude them into bar or tubular shape. In detail, a billet is pushed or drawn through a die of the desired cross-section in hydraulic presses to produce bars, tubes, and a wide variety of profiles with an excellent surface finish, improved mechanical properties, and hollow sections. High-strength magnesium alloys are more difficult to extrude and need to be extruded at higher temperatures and/or lower speeds, thus lower productivity with a greater risk of failure.

While hollow extrusions can be made with a mandrel and a drilled or pierced billet, it is generally more economical (higher productivity) to use a bridge die where the metal stream is split into several branches and recombined before the die exit. **Figure 10** is schematic illustration of the extrusion setup for the semi-hollow, hollow (using port-hole dies), and solid profiles. It should be pointed out that hollow extrusions produced from port-hole dies have solid-state seams (formed during extrusion)

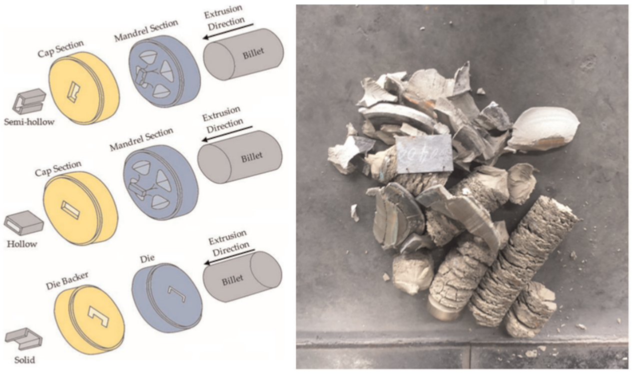


Figure 10.
Schematic illustration of the extrusion setup for the semi-hollow, hollow, and solid profiles (left, [24]) and rare earth-containing magnesium alloy extruded at too high a rate (right).

in the parts. If the components require high-pressure tightness, seamless extrusions produced using mandrel-die are recommended.

Temperature and extrusion rate are two critical parameters for hot extrusion process. They are correlated and strongly dependent on alloy compositions and microstructure of casted billet. For example, 350°C is found to be the optimized temperature in our work to extrude magnesium alloys without rare earth, while those with rare earth require a higher temperature of 400°C. An extrusion rate of 0.6 mm/s is typical for those alloys without rare earth; rates as low as 0.1 mm/s are required for rare-earth magnesium alloys. For development of each new grade as illustrated in Section 2.5, lots of production trials are needed to optimize these two parameters in a costly trial and error process (right, **Figure 10**).

2.5 Grades of dissolvable magnesium

Alloys reported herein cover a wide range of suppliers from the whole dissolvable magnesium industry, including material developed and commercialized internally.

2.5.1 Fast dissolvable alloys

Reaction kinetics are slowed with decreasing well temperature. While the magnesium alloy will eventually dissolve, client requirements of complete dissolution in 15 days force reformulation of alloys. It is simple to take a known alloy and modify the inclusion of impurities that accelerate dissolution. For example, developing AZ31–2 for accelerated dissolution at low-temperature low salinity. Increasing copper by 50% only increased dissolution rate by 36% in AZ31–2A. Increasing the nickel content by 25% in AZ31–2B resulted in an increase of 61%. Increasing both copper and nickel content by 50% for AZ31–2C results in a 115% increase in dissolution rate (**Figure 11**).

The addition of indium to a magnesium-aluminum alloy will also allow for an accelerated corrosion mechanism. Aluminum, despite being a very reactive element, is well known to form a passivating film that makes it corrosion-resistant. Aluminum will inhibit corrosion of magnesium alloys due to the β phase protecting the magnesium matrix phase through a passive surface film. The addition of indium will destabilize the protective aluminum oxide surface film, accelerating the corrosion of the alloy. It has been reported that the indium redeposits back onto the surface, which further deteriorates the film, leading to a corrosion rate increase of 350% in 25°C 3.5% NaCl by adding 3.5 wt% indium [25].

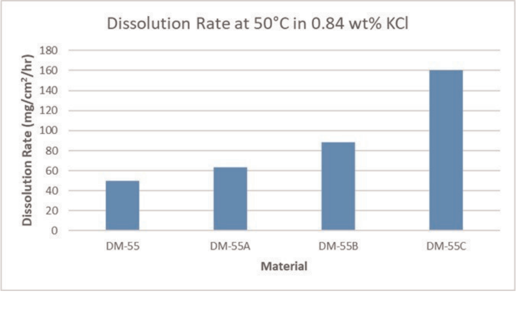


Figure 11.
Dissolution rate response change of a low-temperature magnesium alloy based on AZ31 with increasing noble alloying element inclusion. Measurements performed by CNPC USA.

2.5.2 High-temperature dissolvable alloys

Magnesium experiences a precipitous decline in mechanical properties at 95°C, which is the maximum operational temperature for many US shale wells. Internationally, some shale reservoirs reach temperatures of 175°C, which creates a significant challenge for using dissolvable magnesium (**Figure 12**).

A common solution to stabilize mechanical properties for high-temperature magnesium alloys is to utilize rare earth elements that create secondary precipitates. The addition of rare earth will not only increase the high-temperature stability but also increase the mechanical properties. Apart from the Orowan strengthening of precipitates, strong basal texture and grain size refinement strengthening lead to improved tensile properties at room and elevated temperatures. As previously mentioned, the reaction kinetics accelerate with increasing temperature. Ideally, the number of noble impurities will be decreased to slow the reaction rate to ensure sufficient operational isolation downhole. It can be impractical for manufacturers to manage multiple serializations of a given alloy for various temperatures, so long-duration coatings are often used to provide additional lifetime in situ.

2.5.3 High elongation dissolvable alloys

There exists a need for high elongation alloys, defined as having an elongation of 16 to 28%, for components like foldback rings or metal seals that must deform during the course of setting to support the element or actually create the seal with the casing (**Figure 3**). It is challenging because magnesium has a relatively low ductility due to limited slip planes in the material due to its HCP structure.

An ultra-high elongation magnesium alloy possesses a measured ductility greater than 28%. In our work, Lithium is added to increase ductility with a simultaneous decrease in mechanical strength. Additions of 14% or more lithium will result in a BCC structure that is expressed with high ductility and low mechanical properties. HD-1, HD-2, and HD-3 are high ductility (HD) alloys with no additions of rare earth or lithium. HD-RE-1, HD-RE-2, and HD-RE-3 are high-ductility alloys alloyed with rare earth, without the addition of lithium. **Figure 13** demonstrates the transition starting

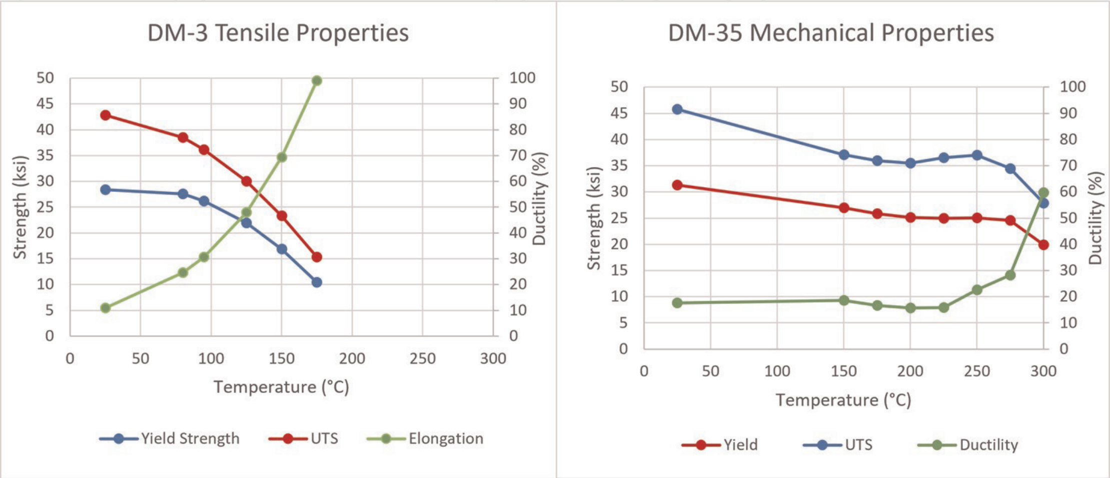


Figure 12.
Degradation of dissolvable magnesium alloy properties as a function of temperature. (left) alloy AZ31–1 formulated without rare earth demonstrates steep strength decline with increasing temperature while (right) alloy with rare earth shows only modest strength decrease even to 300°C. Measurements performed by company CNPC USA.

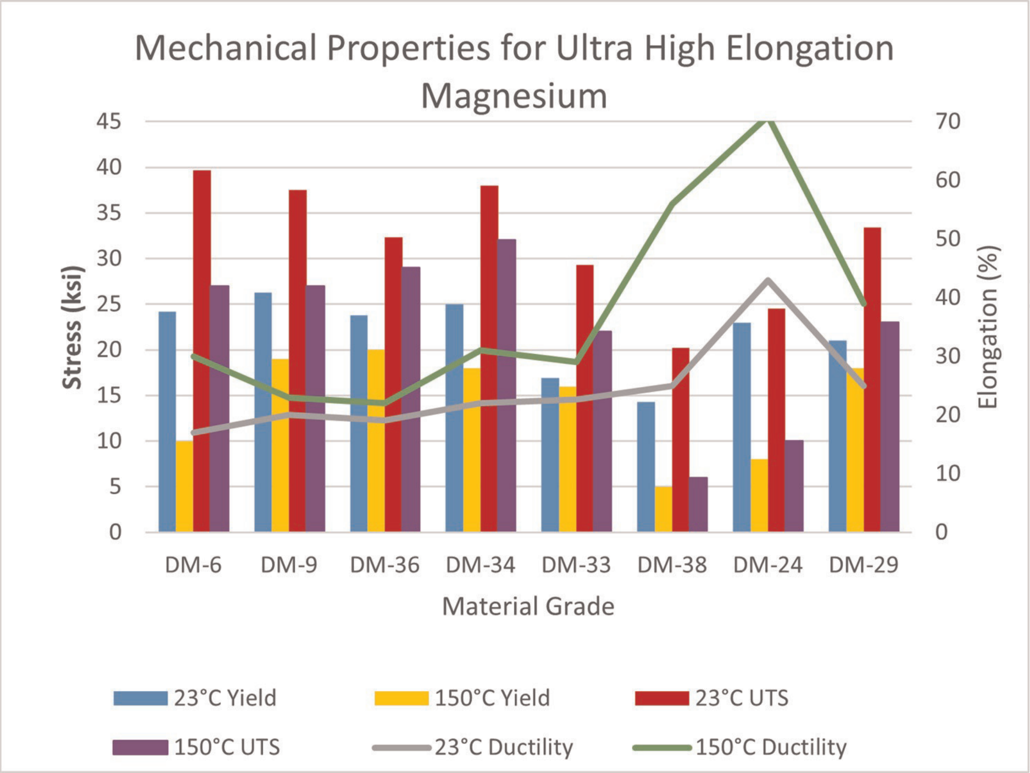


Figure 13.
Plotted mechanical properties of five high elongation magnesium alloys and three ultra-high elongation magnesium alloys. Measurements were performed by CNPC USA.

with a low amount of lithium in UHD-RE-1 that increases in UHD-RE-2. The ductility of UHD-RE-3 decreased despite a similar amount of lithium to UHD-RE-2 due to the addition of more rare earth elements to increase the strength. A passive surface film begins to form, which advantageously slows the corrosion rate for critical high-temperature sealing applications. Additions of yttrium will further reduce the corrosion rate to allow the sealing element to function for the entirety of the fracturing operation. Combining gadolinium and yttrium with lithium and magnesium also leads to particle dispersed strengthening due to phases like Al2Y and microstructure refinement.

3. Dissolvable magnesium failure analysis

Different from conventional Mg alloy, dissolvable magnesium alloy is doomed to “failure”, that is, dissolving. Besides qualifying issues from manufacturing process, for example, material cleanliness, micro-cracks or other defects, quality consistency, etc., most common failure of DM is a selection of grade with unsuitable dissolving rate based on wrong testing method (**Table 1**) or ineffective delay coating (Section 4). DM

Condition (1% KCl, 95°C)	Dissolution rate, mg/cm^2/hour (average)
Autoclave, air	33 ± 1.5
Autoclave, N_2 purge	21.5 ± 1.5
Waterbath	32.6 ± 1.0

Table 1.
Comparison of the dissolution rate of AZ31–1 in the same temperature fluid in three different test methods.

simply dissolves too fast, and parts lost mechanical strength (i.e., over-stressed) due to mass loss before hydraulic fracturing finishes. As one of the pioneering operators to develop extremely high-temperature wells, we also found unique stress corrosion cracking (SCC) failure mode when DM is used at elevated temperatures [26].

During a hydraulic fracture operation in a 125°C shale well in our previous operation, a sudden, premature failure was recorded with a plug utilizing rare-earth magnesium alloys HT-RE-1 and HT-RE-2 (high-temperature grade). Due to the nature of the tool, it could not be retrieved to perform a failure analysis. Tests on high-temperature plugs, made from rare earth-containing magnesium alloys, were performed in simulated well conditions where temperature > 140°C and pressure in tap water at pressures exceeding 50 MPa. A plug with HT-RE-1 slips failed suddenly. Subsequent inspection revealed significant fracturing of the HT-RE-1 slips (**Figure 14**). Repeating the test with HT-RE-2 slips resulted in a similar failure, with close investigation, showing an initial crack in at least one slip formed and propagated early into testing. Testing a plug with HT-RE-1 slips in 140°C oil was successful. Despite very low dissolution rates in unstressed conditions, an unknown mechanism involving tap water caused accelerated corrosion and rapid failure of HT-RE-1 and HT-RE-2.

Scanning electron microscopy (SEM) found characteristics of stress corrosion cracking (SCC). A nonobvious alloy, HT-RE-3, was selected as a potential replacement due to the higher elongation, despite a lower yield. Slow strain rate testing (SSRT) was performed in 140°C tap water at a rate of 4.00×10^{-6} in/in/s for HT-RE-1, HT-RE-2, and HT-RE-3 (ASTM G129), there is a substantial decline in mechanical properties when conducting SSRT at 140°C when compared to the results from standard tensile testing at 140°C (**Figure 15**). The extreme decrease in ductility demonstrates water is the factor accelerating the fracture via SCC [26]. Subsequent 140°C tap water plug testing with HT-RE-3 slips was crack-free and successful. A clear

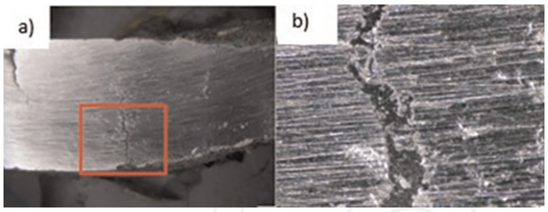


Figure 14.
A cross-sectioned fractured HT-RE-1 slip with (a) an evident crack and (b) a closeup of the fracture.

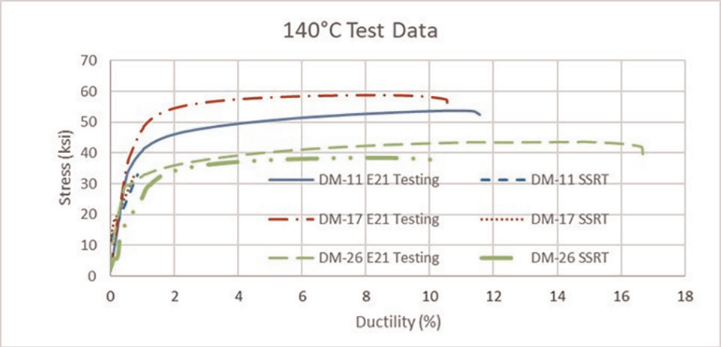


Figure 15.
Comparison of high-temperature tensile testing to SSRT at 140°C for HT-RE-1, HT-RE-2, and HT-RE-3. HT-RE-1 and HT-RE-2 experienced a precipitous decline in properties, whereas only a moderate decline in mechanical properties was measured in HT-RE-3. Measurements were performed by CNPC USA.

relationship between SCC, material microstructure, and chemical formulation was established so that a new grade of alloy with well-designed microstructure was developed to avoid SCC and successfully prevented sudden cracking issues of HT dissolvable plugs used in ultra-HPHT shale well development.

4. Protection and coating for dissolvable magnesium

During field application, degradable plugs are required to keep mechanical integrity under high stress during hydraulic fracturing process in the first 6–24 h (depending on operation design) and to be dissolved as quickly as possible without large solid residual to put wells into production quickly (i.e., high operation efficiency). The former requirement demands DM to have lower dissolving rate so that plug can maintain reliable strength during operation, while the latter requires DM to have dissolving rate as high as possible. A conflicting requirement leads to two kinds of broadly observed failure in field, either "premature" disintegration or not dissolving at all at the end due to wrapping of oily contamination when dissolving rate is too low [27]. To circumvent these contradictory requirements for the DM alloys, delayed surface coating (or "temporary coating"), such as polymer spray coating, has been utilized on a fasting dissolving DM (typically >20 mg/cm^2/hour) to delay its initial dissolving process.

Since all polymers are permeable to gas or water molecules to certain level [28], for immersion application, the rate of base metal corrosion where such coatings are used should not exceed approximately 1.3 mm/year (50 mils/year) according to industrial standards [29]. For typical magnesium DM, corrosion rate is several orders of high than this criteria, and ordinary coatings (typically <500 μm) are doomed to be unreliable. Liner (>2 mm) or inorganic cladding might be an option, but they are typically too thick to protect complex DM parts with tight tolerance in real applications. Since delay coating is just "temporary" (i.e., 6–24 hours.), it is still an effective option as long as coating materials and application process are well-engineered and broadly tested. Since DM plug technology in oil and gas is mainly led by companies, this section will illustrate industrial's common practice of delayed coating on DM plugs, especially the application experience from author's group.

4.1 Low-to-medium temperature coating technology

Low-to-medium temperature typically means the temperature at which DM alloy does not deteriorate in mechanical strength (typically <120°C). Ductility of these DM grades can be typically maintained above 8%, that is, categorized as ductile material in oil and gas industry [28] since heavy precipitation enhancement can be avoided. In this scenario, DM typically fails in the form of general corrosion (i.e., gradual material loss), instead of catastrophic crack failures such as stress corrosion cracking or hydrogen embrittlement. It has a low requirement on coating quality as long as it can provide barrier effect to certain level. Therefore, delay coating that is found effective in protecting DM plugs is typically cost-efficient polymers, such as acrylic, epoxy, and polyurethane, or their combinations. Their selection and coating parameters depend on the downhole environments, including temperature, pressure, fluid salinity, etc., and they are typically trading secrets for each service provider. For example, Kumar et al. reported the usage of phenolic-based and aliphatic-based epoxy on their dissolving Mg products to delay disintegration [30].

The only concern for these spray coatings is uneven protection on different geometries. As reported by Zhao et al., for a typical failure process, coating first breaks at an edge or corner, where coating thickness is typically low (**Figure 16b**) or full of defects such as holidays and pinholes [31]. Fluids then not only corrode the exposed DM substrate immediately under these areas but more importantly infiltrates between the coating/DM interface in the form of film filiform corrosion (Under-film Corrosion, **Figure 16a**), causing material loss. Finally, blistering occurs all over the coating and causes complete breakage of the coating. Therefore, DM parts with sharp edges or corners fail much quicker than those with only smooth surface area (e.g., fracture ball, **Figure 3**), special effort, either an advanced coating or strip coating, needs to be applied to these difficult areas [32] to prevent "premature" disintegration on certain complex parts.

4.2 High-temperature coating technology

In stark contrast to low-temperature fail mechanism, DM alloy typically fails in the form of environmental assistant cracking (EAC) at high temperatures (usually >120°C), instead of a predictable general corrosion process. As discussed above, mechanical strength of traditional Mg alloys typically drops significantly around 120°C due to the degradation of dispersion phases. To maintain reasonable strength (>270 MPa) for high temperature (>140°C) DM plug applications, the so-called HT grades are heavily precipitation-enhanced through rare earth microalloying at cost of alloy ductility [27, 28]. Even though the detailed cracking mechanism, such as stress corrosion cracking (SCC), hydrogen embrittlement (HE), and formation of hydride, is still under debate, however, it is unanimously believed that the loss of elongation of HT grades (typically drop from 15–20% to 5–12%) make that material more susceptible to SCC failures [33–35]. Based on industrial standards [35] and various research [36], coatings, especially organic coating, cannot eliminate the SCC of base metal due to inevitable film defects and gas/moisture permittivity, but it is still an effective option as delay coating, if the stressed DM parts are efficiently isolated from the service environment for 6–24 hours.

Grease and thin polymer coating have been reported to have a synergistic effect to address EAC issue of DM by Zhao et al. [27]. In this combination, HT grease is applied on top of thin polymer coatings, for example, epoxy coatings, silicone coatings, and fluoropolymer coatings, to cover any defects (pinholes, holidays, etc.) within (**Figure 17a**). The effectiveness of this combination was proven by SSRT at 140°C as shown in **Figure 17b**. Compared with the uncoated sample, this coating increased cracking strength from 200 MPa to 352 MPa (76% increase) and doubled elongation (from 0.9–2%). Based on test results it is believed that below a certain strain range,

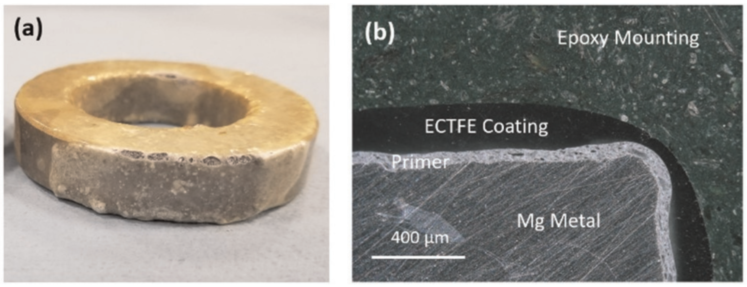


Figure 16.
Photo of (a) failed polymer coating after aging and (b) OM image of ECTFE coating at sample edge area [31].

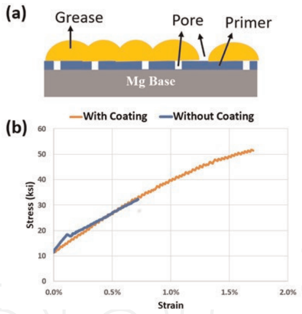


Figure 17.
Schematic illustration of (a) synergistic effect between grease and polymer coating and (b) its effectiveness examined by SSRT. figure reproduced with permission from TMS [27].

the grease coating can prevent SCC of Mg alloy by isolating it totally from corrosive fluids. After further deformation, the grease coating breaks, leaving bare areas unprotected for SCC to initiate. The key technology of this technology is suitable grease material formulation or section (i.e., high-temperature rating, proper consistency, high bonding strength to both metal and polymer base, hydrophobic, with excellent thermal/chemical resistance, and resistant to shearing and impacts, etc.), and its compatibility with polymer coatings. This method is broadly accepted by fields also because of its high “flexibility” in delay time; thicker grease coating always leads to longer delay time, which could provide the operators with a choice at the last-minute change to accommodate unpredictable field requirements if they choose to apply final greasing step on job site manually. This could lead to a significant cost reduction from the perspective of supply chain management.

Given its effectiveness in preventing EAC, grease/polymer combination has been found by Zhao et al., not powerful enough to deal with extremely corrosive environments (i.e., reduced delay time), and extra layer protection is necessary [38]. In his work, failure analysis of grease/polymer combined coatings shows that blistering still occurs near its end stage, therefore, an extra inorganic layer (i.e., surface pretreatment) needs to be added, not only to provide extra barrier but most importantly to prevent filiform corrosion (thus blistering). Among these inorganic coatings, plasma electrolytic oxidation (PEO) coating is tested to be the most effective solution thanks to its dense protective inner layer, high mechanical strength, and most importantly strong affinity to polymers because of its porous top profiles. Since both inorganic PEO layer (15–25 μm) and polymer coating can be controlled thin enough not to interfere with tool assembly and function. Failure analysis on broken areas showed that the blistering issue had been eliminated, and delay time can be doubled due to the existence of inorganic PEO pretreatment [37].

5. Outlook and future direction for dissolvable magnesium

Dissolvable magnesium plugs have had a proven field history over the past decade. Intense effort in dissolvable magnesium alloy development has advanced magnesium alloying and processing as a whole. Driven by several factors like increasing production of oil & gas, the dissolvable frac plugs market size is projected to reach an estimated value of US$ 1178.8 million in 2024 [38]. As more applications are found for DM than hydraulic plugs, oil & gas industry could become of major consumption section of global Mg production. In less than two decades, DM technology evolves from a concept in lab to a commodity with hundreds of commercial grades. This unique application is obviously a success story to take full advantage of high reactivity of Mg materials. However, there is still lot to be done to further advance this technology.

To deal with increased scarcity of traditional easy oil/gas resources, whole industry moving to more HTHP and unconventional reservoirs, where DM fails in the form of stress corrosion cracking instead of general corrosion process, as illustrated in Chapter 5. High strength and ductility must be achieved simultaneously for this scenario, which has been a significant challenge for current DM industry and requires intensive research effort on both formulation and processing. The most cost-efficient route is still exploring new alloying element systems to form effective precipitation phase. It has been under intensive R&D by both industrial and academic communities [39]. The difficulty of this route is forming thermal stable precipitation phase, which typically requires usage of expensive rare earth elements. Rare earth-free micro alloy technology is reported but its performance is not satisfactory. An alternative route is directly adding advanced filers, with different sizes and geometries, to form the so-called composite or nanocomposite materials [40]. These fillers include but are not limited to inorganic powders (SiC, Al_2O_3, TiO_2, etc.), nanotubes, graphene, etc. Significantly improvement has been reported in various research papers, but this technology is not ready for industrial application because of not only cost but also manufacturing difficulties. It is very challenging in manufacturing scale-up to mix fillers, especially in nanosized, uniformly into DM melt, and solidify/cast them without filler aggregation or introducing defects [41], such as voids, cracks, and detrimental inclusions. PM is a more controlled route to address this issue but has proven to be unsuitable technology due to its low ductility and high cost in mixing. Therefore, more efforts need to spend to scale up the composite fabrication technology from material lab to manufacturing line in mill. The last but least technical route is advanced plastic-deforming technology to reduce current grain size of DM significantly, which obviously increases strength and ductility at same time without modifying formulation. However, these technologies, such as equal channel angular extrusion (ECAE) and friction stir extrusion [42], are still limited to lab research, and there is a long route before industrialization.

In the field application, the by-product of Mg dissolving process, that is, $Mg(OH)_2$, reacts with downhole silicate (either from formation or hydraulic frac sand) to form hard magnesium silicate or aluminum silicate if Al is used as alloying element [43]. The basic mechanism is still under investigation, but formation of this so-called recrystallized material is detrimental to dissolvable plug application because it either warp around DM to prevent it from dissolving or forms a strong cement block *in situ*, blocking the well bore. This recrystallization is strongly related to downhole temperature and fluid conditions and is found even severe in HTHP wells. For example, over 60% failure rate of DM plugs is reported in developing a high-temperature gas well recently, which makes DM plus unsuitable to use. Therefore, a new formulation or dissolving mechanism needs to be developed to prevent recrystallization reaction downhole.

After two decades of intensive R&D on 3D printing technology worldwide, this technology is mature for oil and gas applications from both performance-wise and cost-wise. Various downhole tools and parts are reported to be manufactured from industrial 3D printing process [44], as it brings obvious benefits, such as reduced size (i.e., eliminating joints or connections) and complex shapes not achievable by traditional machining. Given many works have been published in 3D printed Mg alloy

[45], especially dissolvable Mg alloys used in biomedical fields, there is no 3D printing of dissolving metal reported so far in oil & gas industry, probably due to recent downside of the oil market. More R&D efforts need to be invested to bring these benefits to DM downhole tools.

Acknowledgements

The authors would like to thank the management of CNPC USA for granting the permission to publish this work.

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References

[1] Saltzman D. The art of distillation and the Dawn of the hydrocarbon society. Bulletin for the History of Chemistry. 1999;**24**:53-60

[2] Höök M, Hirsch R, Aleklett K. Giant oil field decline rates and their influence on world oil production. Energy Policy. 2009;**37**:2262-2272. DOI: 10.1016/j.enpol.2009.02.020

[3] IEA. World Energy Outlook 2020. Paris: IEA; 2020. License: CC BY 4.0

[4] Andreas J. The shale revolution in the U.S. and its impact on energy markets, energy security, and the U.S. energy transition. In: International Report of the Konrad-Adenauer-Stiftung. Berlin: Konrad-Adenauer-Stiftung; 2015

[5] Helms D. Horizontal Drilling. North Dakota Department of Mineral Resources Newsletter. 2008;**35**:1-3

[6] U.S. Government Accountability Office. Oil and Gas Information on Shale Resources, Development, and Environmental and Public Health Risks. U. S. Government Accountability Office; 2012

[7] Durey A, Degner D. Bridge-plug Millout with coiled tubing-case histories. In: Paper Presented at the SPE/ICoTA Coiled Tubing Roundtable. Houston, Texas. Richardson, Texas: SPE; 2000

[8] Walton Z, Fripp M, Porter J, Vargus G. Evolution of Frac plug technologies – Cast iron to composites to dissolvable. In: Paper Presented at the SPE Middle East Oil and Gas Show and Conference. Manama, Bahrain. Richardson, Texas: SPE; 2019

[9] Xu ZY, Zhang ZH. The art of disintegration – Ten years in review of disintegrable metals and downhole tools. In: Paper Presented at the Offshore Technology Conference. Houston, Texas. Richardson, Texas: SPE; May 2019

[10] Xu ZY, Agrawal G, Salinas BJ. Smart nanostructured materials deliver high reliability completion tools for gas shale fracturing. In: Paper Presented at the SPE Annual Technical Conference and Exhibition. Denver, Colorado, USA. Richardson, Texas: SPE; October 2011

[11] Fripp M, Walton Z. Degradable metal for use in a fully dissolvable Frac plug. In: Paper Presented at the Offshore Technology Conference. Houston, Texas, USA. Richardson, Texas: SPE; May 2016

[12] Zhang P, Chunsheng P, Jingyang P, Wang Z. Study and field trials on dissolvable Frac plugs for slightly deformed casing horizontal well volume fracturing. ACS Omega. 2022;**7**: 10292-10303. DOI: 10.1021/acsomega.1c06928

[13] Gradl C. Review of recent unconventional completion innovations and their applicability to EGS Wells. In: Proceedings of 43rd Workshop on Geothermal Reservoir Engineering. Stanford, California: Stanford Geothermal Program; February 2018

[14] Galvanic series noble metals By Tugsataydin – Own work (CC BY-SA 4.0) via Commons Wikimedia

[15] Hu H, Nie X, Ma Y. Corrosion and surface treatment of magnesium alloys. In: Czerwinski A, editor. Magnesium Alloys Properties in Solid and Liquid States. London, UK, London, UK: Intechopen; 2014. DOI: 10.5772/58929

[16] Sherman A, Doud B, Farkas N, Manufacture of controlled rate

dissolving materials, US Patent # 9,757,796, September 12, 2017

[17] Sherman A, Doud B, Farkas N, Galvanically-active in situ formed particles for controlled rate dissolving tools, US Patent # 9,903,010, February 27, 2018

[18] He SM, Peng LM, Zeng XQ, Ding WJ, Zhu YP. Comparison of the microstructure and mechanical properties of a ZK60 alloy with and without 1.3 wt.% gadolinium addition. Materials Science and Engineering A. 2006;**433**:175-181. DOI: 10.1016/j.msea.2006.06.063

[19] Pourbahari B, Emamy M, Mirzadeh H. Synergistic effect of Al and Gd on enhancement of mechanical properties of magnesium alloys. Progress in Natural Science: Materials International. 2017;**27**:228-235. DOI: 10.1016/j.pnsc.2017.02.004

[20] Liu Y, Yang Y, Yi M, Yu J, Li B, Zhang Z. The formation of 14H-LPSO in Mg-9Gd-2Y-2Zn-0.5Zr alloy during heat treatment. Materials (Basel). 2021;**14**(19):1-13, 5758. DOI: 10.3390/ma14195758

[21] Davis J. Metals Handbook Desktop Edition. 2nd ed. Materials Park, OH: ASM International; 1998

[22] Patel D. "Downhole dissolvable plug", US Patent 8,276,670 B2. October 2, 2012

[23] Grandfield JF. Direct chill casting of magnesium extrusion billet and rolling slab. In: Bettles C, Barnett M, editors. Advances in Wrought Magnesium Alloys. Sawston: Woodhead Publishing; 2012. 229 p. DOI: 10.1533/9780857093844.2.229

[24] Qamar SZ, Pervez T, Chekotu JC. Die defects and die corrections in metal extrusion. Metals. 2018;**8**:380. DOI: 10.3390/met8060380

[25] Wang XW, Wang W, Chen W, Chen DM. Effects of indium on corrosion behavior of Mg-Al-Cu alloy. Materials Characterization. 2021;**177**: 111157. DOI: 10.1016/j.matchar.2021.111157

[26] Dunne TR, Yue WH, Zhao L, Nettles D, Cheng P, Ren JX, et al. Addressing corrosion stress cracking issue of magnesium Frac plugs used in ultra HPHT shale well development. In: Paper Presented at the Abu Dhabi International Petroleum Exhibition & Conference. Abu Dhabi, UAE. Richardson, Texas: SPE; November 2021

[27] Zhao L, Yue WH, Ren JX, Dunne TR, Cheng P, Liu HL. Flexible surface treatment technology to enable temporary SCC prevention for Mg dissolvable alloys. In: Proceedings of Magnesium Technology 2022; 05 February 2022. New York: Springer; 2022. pp. 241-248

[28] Heidersbach R. Metallurgy and Corrosion Control in Oil and Gas Production. 2nd ed. Chichester: Wiley; 2011. DOI: 10.1002/9780470925782

[29] Bahadori A. Essentials of Coating, Painting, and Lining for the Oil, Gas and Petrochemical Industries. Amsterdam: Elsevier; 2015. DOI: 10.1016/C2013-0-19127-1

[30] Kumar D, Hernaez ED, Sanchez JS, Xu ZY. Temporary coating for dissolving Frac-balls used in multi-stage fracturing systems. In: Paper Presented at the Offshore Technology Conference. Houston, Texas, USA. Richardson, Texas: SPE; April 2018

[31] Zhao L, Song Y, Dunne T, Ren JX, Yue WH, Yang L, et al. Advanced compound coating for delaying corrosion

of fast-dissolving alloy in high temperature and corrosive environment. International Scholarly and Scientific Research & Innovation. 2021;**15**:71-75. DOI: 2021

[32] Tekumalla S, Seetharaman S, Almajid A, Gupta M. Mechanical properties of magnesium-rare earth alloy systems: A review. Metals. 2014;**5**:1-39. DOI: 10.3390/met5010001

[33] Xu DK, Han EH, Xu YB. Effect of long-period stacking ordered phase on microstructure, mechanical property and corrosion resistance of Mg alloys: A review. Progress in Natural Science. 2016;**5**:117-128. DOI: 10.1016/j.pnsc.2016.03.006

[34] Song GL, editor. Corrosion of Magnesium Alloys. Amsterdam: Elsevier; 2011. p. 299

[35] NACE MR 0175/ISO15156-1:2020. Petroleum, Petrochemical, and Natural Gas Industries-Materials for Use in H2S-Containing Environments in Oil and Gas Production. Houston: NACE; 2020

[36] Srinivasan PB, Blawert C, Dietzel W, Kainer KU. Stress corrosion cracking behavior of a surface-modified magnesium alloy. Scripta Materialia. 2008;**59**:43-46. DOI: 10.1016/j.scriptamat.2008.02.032

[37] Zhao L, Dunne T, et.al. Route to optimize temporary seal for downhole dissolvable magnesium plug application in HT: Failure analysis and learnings. Paper Presented at AMPP Annual Conference and Expo. Denver, USA. Houston, TX: AMPP; Mar 2023

[38] Stratview Research. Dissolvable Frac Plugs Market Size, Share, Trend, Forecast, & Competitive Analysis: 2019-2024. Jun, 2019. Available from: https://www.stratviewresearch.com/491/dissolvable-frac-plugs-market.html

[39] Saal JE, Wolverton C. Thermodynamic stability of Mg-based ternary long-period stacking ordered structures. Acta Materialia. 2014;**68**:325-338. DOI: 10.1016/j.actamat.2013.10.055

[40] Nie KB, Wang XJ, Deng KK, Hu XS, Wu K. Magnesium matrix composite reinforced by nanoparticles – A review. Journal of Magnesium and Alloys. 2021;**9**:57-77. DOI: 10.1016/j.jma.2020.08.018

[41] Surappa MK. Microstructure evolution during solidification of DRMMCs (discontinuously reinforced metal matrix composites): State of art. Journal of Materials Processing Technology. 1997;**63**:325-333. DOI: 10.1016/S0924-0136(96)02643-X

[42] Shunmugasamy VC, Khalida E, Mansoor B. Friction stir extrusion of ultra-thin wall biodegradable magnesium alloy tubes -microstructure and corrosion response. Materials Today Communications. 2019;**26**:102-129. DOI: 10.1016/j.mtcomm.2021.102129

[43] Li M, Chen L, Wei R, Liao CL, Fu T. The application of fully dissolvable Frac plug technique in Weiyuan Gasfield. In: Paper Presented at the SPE Kingdom of Saudi Arabia Annual Technical Symposium and Exhibition. Dammam, Saudi Arabia. Richardson, Texas: SPE; April 2018

[44] Deng GJ, Kendall A, Wakefield J. The ultra-expansion completion packer integrated with additive manufacturing technology. In: Paper Presented at the SPE Annual Technical Conference and Exhibition. Dallas, Texas, USA. Richardson, Texas: SPE; September 2018

[45] Karunakaran R, Ortgies S, Tamayol A, Bobaru F, Sealy MP. Additive manufacturing of magnesium alloys. Bioactive Materials. 2020;**5**:44-54. DOI: 10.1016/j.bioactmat.2019.12.004