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Use Of Eutectic Metal Alloys to Seal Problematic Permeable Formations

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Abstract

Experiments were conducted to evaluate the penetration of melted Bismuth metal alloys into potentially troublesome formations such as depleted zones or low to medium lost circulation zones in sandstone and carbonate rocks for the purpose of sealing and strengthening those zones. Sandstone and carbonate cores were saturated with a light brine by flowing through the core at temperature of 150°C. After brine saturation, melted alloy metal was then displaced into the core bottom up displacing the brine. Once the melted alloy was detected to have reached the top of the core. The flow was stopped and allowed to cool. The core was then removed and gas and liquid permeability, tensile strength and triaxial measurements were done and compared to the baseline. The results demonstrated that intrusion of the melted alloy into the rock reduced the permeability, increased the tensile and compressive strength. Previous work has utilized polymeric materials for the preferential sealing of zones to prevent pressure communication between zones. For the most part the use of polymeric materials has been limiting due to viscosity, temperature, and potential degradation issues. Metal alloys when melted have similar viscosity to water and when placed in the right temperature regime will not degrade. In addition, with solidification volume expansion, 1-2% does occur which enables superior sealing.

Introduction

Lost circulation is one of the major drilling challenges in the industry. It results in significant nonproductive time and cost due to packoffs, stuck pipe, and most importantly well-control events. Of course, the loss of drilling fluid can be expensive but, for the most part, it is the least significant of the potential impacts of lost circulation.

Lost circulation can have many causes, but it is frequently a direct result of wellbore pressure that is too high and thus exceeds the fracture gradient. This increase in wellbore pressure can be the result of static drilling fluid weight that is too high and the resulting high equivalent circulating density (ECD) due to narrow annuli, increase in mud weight, increase in pump rate, and/or increases in viscosity which might result from solids loading. The problem is frequently exacerbated by production zones that are pressure depleted resulting in the reduction of the fracture gradient. This scenario typically results in lost circulation. Another scenario is when the highly fractured normally pressured zone is exposed to a high overbalance resulting in pressure transmission into the formation resulting in borehole failure and potential loss of productive time. The use of eutectic metal alloys to mitigate such scenarios is demonstrated in this study. Penetration into the formation of a melted alloy that become structural solid upon cooling can prevent pressure communication into the formation and strengthen the rock.

Natural fractures-vugs can result in significant loss. These in many ways are the most difficult to manage because in many cases the number of options available to remediate the losses are limited to pumping in pills with the hopes of sealing off the losses. These can range from being relatively low losses to total losses depending upon the size and extent of the fracture-vug. It is these latter scenarios that Aramco typically has difficulty in managing resorting many times to accepting the loss fluid or converting to mud cap drilling.

Based on the rate of fluid loss, lost circulation can be divided into the following categories (Rabia, 2002):

- Seepage: < 10 to 15 barrels per hour
- Partial: 10 to 50 barrels per hour
- Severe: >50 barrels per hour

Mitigation

Reducing drilling fluid density, or mud weight as it is commonly known, might seem to be a reasonable option, but drilling through non-depleted zones or normally pressured low-permeability zones, such as shales, will most likely minimize the ability to control lost circulation by using such a dramatic option. Lowering the ECD is the most reasonable preventive measure that can be utilized. This can be done by lowering the pump rate which, will in turn, negatively impact cuttings transport and make things worse, or lowering the drill solids content and thus reduce the overall viscosity.

Wellbore strengthening (WBS) techniques have been developed as a technique for mitigating lost circulation for many years (Alberty and McLean, 2004). The concept of WBS was initially to plug and seal incipient fractures by using sized

particles that prevent fracture propagation. However, over the years, different mechanisms have been proposed. As suggested by Alberty and McLean (2004), plugging and sealing incipient fractures is one of those mechanisms.

Wellbore stress augmentation (WSA) functions by altering the hoop stress or closure stress near the wellbore by propping open the incipient fractures and thus maintaining a higher hoop stress that must be overcome before propagation of fractures from the wellbore can occur. The last mechanism is referred to as the Fracture Propagation Resistance – particles plug off leaks at the fracture tip and prevent pressure communication to the fracture, thus preventing propagation. The 2014 paper by van Oort and Razavi suggested that this is the most viable mechanism for mitigating fracture growth.

Understanding the width of the induced fracture is essential to achieving this goal. Alberty and McLean (2004) and Zhang et al. (2016) attempted to calculate fracture width primarily utilizing mechanical loading, i.e., stresses and rock mechanical properties assuming isothermal conditions. These days most service providers and many operators have software packages which will not only estimate fracture width but also predict the particles sizes and quantities of LCM needed to control lost circulation. These calculations incorporate multiple assumptions ranging from changing stresses based on depth in the wellbore to changing drilling fluid parameters (e.g., static fluid weight, ECD), to various lithologies and, of course, temperature.

When designing particle-size treatments, it is important to separately characterize each section of the hole to get the most engineering benefit possible from the particles. Regardless of the mechanism chosen for WBS, particle sizing is key but not the only requirement. To ensure reduced pressure communication to the tip of the fracture, it is important to have the appropriate distribution of particles to assure a good low-permeability plug to seal the fracture.

Wellbore strengthening materials (WSM) packages are typically designed with a particle size distribution (PSD) that accounts for the apparent fracture width and rate of drilling fluid loss. To maximize the impact of that package, the Ideal Packing Theory (Dick et al., 2000; Abrams, 1977; Amer et al, 2016) must be included in the design. This theory has led to attempts to design a wellbore geometry model (WGM) package that would include coarse and fine particles. The coarse particles must be sufficiently coarse to plug or bridge the mouth of the fracture or oversized pores in the high-permeability formation. The finer particles form a low-permeability plug to plug or bridge the fracture. Together the distribution of particle sizes creates a seal that also provides good filtration control. This concept is the foundation of modern WSM packages as designed and executed today.

As stated above, initial models estimating fracture width were based on isothermal conditions. Most recently Yao and Alberty (2020) examined the effects of temperature on wellbore strengthening. They concluded that a contrast in temperature of the drilling fluid and the formation will affect the near wellbore stresses. In addition, in calculating incipient fracture widths, it is important to consider these thermal effects. This effect should also

be considered when designing WBS treatments which are based on expected fracture widths. Failure to do so can result in failure of the WBS treatment.

Hoxha, et al. (2016) demonstrated that a thermal effect might be used to improve the apparent fracture gradient thus minimizing the chance of lost circulation by using good thermal wellbore strategies. Hoxha and team designed coated exothermal particles that can be thought of as time-release capsules such that when a pill containing these time release capsules is placed at the interval most likely to fracture, the coated particles will enter the fracture and initiate an exothermic reaction. Thus, heating the wellbore and increasing the fracture gradient by several hundred psi.

Remediation

Once an induced or natural fracture is actively losing fluid, losses can be severe with hundreds of barrels of drilling fluid loss in a short period of time which can result in several negative impacts including loss of well control. A vast number of materials and strategies have been developed to remediate lost circulation.

There are many different types and particle sizes used as lost circulation materials (LCM). LCM products include both organic and synthetic man-made materials. Typical examples of lost circulation materials are flakes, particles, and fibers. Chemically these lost circulation materials include calcium carbonates (particulate or flake), crushed mica (typically flake), and graphite and dolomites (particles). Various plant materials that have been used include kenaf, walnut hulls, peanut hulls, coconut coir, and grape pomace. Various carbohydrate polymers such as starches are available.

There are also a variety of synthetic materials available that can be used to increase viscosity. Typically, these are high-molecular-weight polymers that upon wetting become viscous.

Additives which physically plug or seal the losses, include flaked cellophane, sawdust, and gypsum. Shredded newspaper and cottonseed hull are other popular choices to help plug the losses. The latter two are usually used only when water-based systems are in use.

No matter the material, most strategies work from the physical principles of providing:

a) A structural integrity by establishing a network of particles, flakes, and fibers that form a mesh. The key is for that mesh to have integrity once the base fluid (water or oil) is squeezed out of the matrix.
b) Another process is to provide viscosity such that with wetting or shearing, the viscosity is so high as to slow the losses into the fracture.
c) The third strategy is simply a combination of a and b.

Eutectic Metal Alloy

Eutectic brazing alloys are a distinct group of alloys that combine the bonding characteristics of the component metals

with the superior flow properties of pure metals. Eutectic alloys melt and solidify at the same temperature. This instantaneous phase change from solid to liquid makes eutectic alloys free-flowing and ideal for a wide range of electrical, electronic, and plumbing manufacturing applications. Eutectic metal alloys offer a unique treatment for lost circulation that can be customized and formulated to change state at specific temperatures as dictated by the specific downhole environment.

Eutectic is defined as an isothermal reversible reaction in which a liquid solution is converted into two or more intimately mixed solids on cooling; the number of solids formed being the same as the number of components in the system.

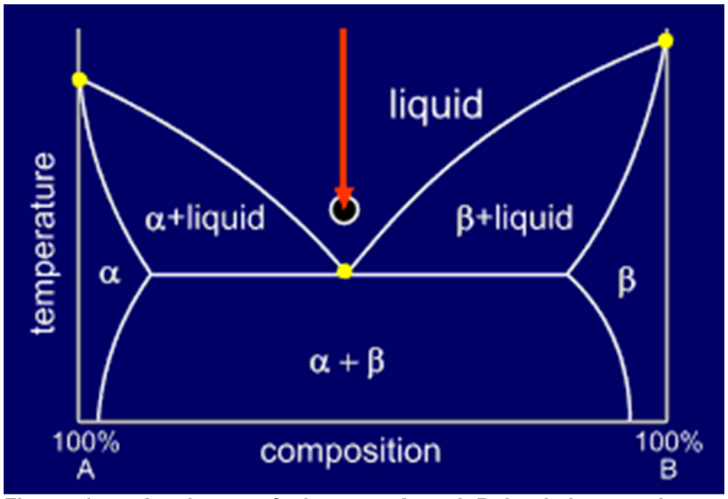

Figure 1: A mixture of elements A and B in their eutectic proportions at a temperature high enough to melt both elements.

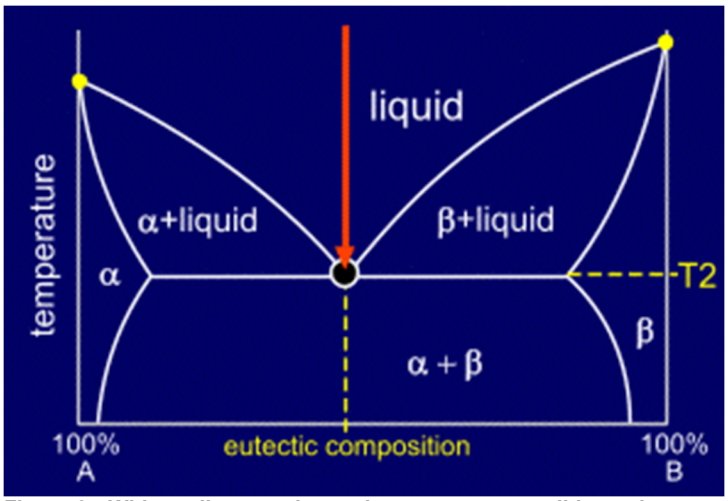

Figure 2: With cooling, no change in state occurs until it reaches temperature T2, where it starts to solidify at any favorable nucleation sites.

When the eutectic composition solidifies, it forms alternating layers of the composing metals A and B. The layers are thin – approximately 1 μm thick. The "stripy" microstructure is known as a lamellar microstructure.

As cooling continues, the existing nucleation sites will grow, adding more A and B molecules to respective layers.

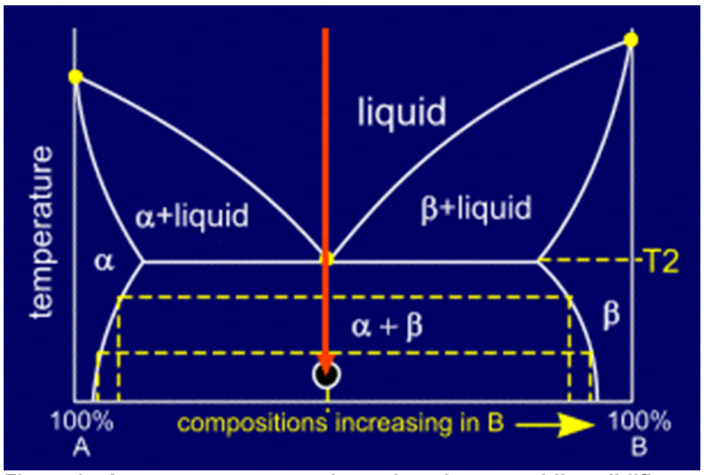

Figure 3: At some temperature the entire mixture rapidly solidifies into a *eutectic solid*.

Evaluating the phase diagram, the compositions of A and B change with temperature. Even though the alloy is now a solid, the composition of the layers will continue to change via diffusion as the metal cools. Of significance is that the eutectic composition and state will vary as a function of the temperature of the solid.

Bismuth Alloys

In this paper we are focused on the use of bismuth and bismuth-tin alloys for sealing microfractures and matrix rock. There are several sources in China, Canada, and the U.S. of bismuth-tin alloys with varying melting temperatures. The alloy we have been working with is Bismuth Tin Alloy 138°C. It has the following mechanical properties.

Table 1: Bismuth Tin Alloy 138°C	
Young's Modulus in Tension at 65°C	$E_{tensile}$ = 21 GPa
Young's Modulus in Compression at 65°C	$E_{compressive}$ = 1.8 Gpa
Poisson's ratio at room temperature	υ = 0.35
Bulk density at room temp	ρ = 8.6 g/cm^3 (0.309 lb/in^3)
Compressive 0.2% offset Yield Strength at 65°C	Rp02 = 38 MPa

Although we have not worked with Bismuth Tin Alloy 263, the expectation is that we will for higher temperature applications.

Table 2: Bismuth Tin Alloy 263ºC	
Young Modulus Tension at 90°C	$E_{tensile}$ = 34 GPa
Young Modulus in Compression at 90°C	$E_{compressive}$ = 1.6 GPa
Poisson's ratio at room temperature	υ = 0.36
Bulk density at room temp	ρ = 9.8 g/cm^3 (0.352 lb/in^3)
Compressive 0.2% offset Yield Strength at 90°C	Rp02 = 25 MPa

There are other alloys that melt at 95°C and 124°C, which for lower temperature applications, may be appropriate. We have not worked with these alloys either.

China is a resource of several alloys. My expectation is that we will be looking at all of these alloys to determine if there are any unique attributes we should leverage to our advantage. Table 3 highlights the melting points of a few bismuth-tin eutectic metal alloys.

Table 3: Eutectic Metal Alloys	
Melting Point	Composition
47°C	Pb, Sn, Bi, Cd
70°C	Pb, Sn, Bi, Cd
100°C	Pb, Sn, Bi
138°C	Sn, Bi

Methodology

Core Testing

An experimental apparatus was designed to allow for the injection of molten bismuth into a core under isostatic stress at a temperature of 155°C.

Test Equipment

Testing was performed at 600-psi net effective stress with 1000-psi confining pressure and 400-psi back pressure. Injection was at constant rate of 0.02 mL/min with pressures monitored by 0.02% accuracy transducers. Electrical resistance of the sample was monitored using an AC LCR (inductance (L), capacitance (C), and resistance (R)) meter @ 1-kH frequency to monitor bismuth entry and breakthrough times. A schematic of the setup is shown in Figure 4. The actual setup is shown in Figure 5.

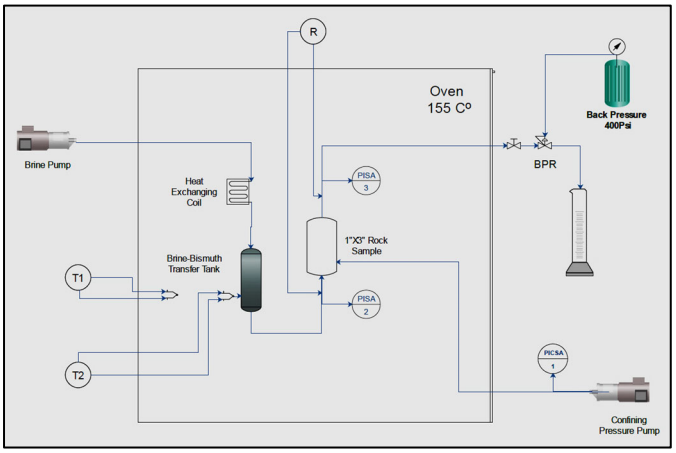

Figure 4: Schematic of setup to monitor electrical resistance for molten bismuth into a core.

Figure 5: Photograph of experimental setup shown in schematic (Figure 4).

Test Injection Procedure

The system was heated to 155°C and allowed to equilibrate overnight to ensure isothermal conditions. Testing was performed at 600-psi net effective stress with 1000-psi confining pressure and 400-psi back pressure. Injection started at constant flow rate of 0.02 mL/min. Resistance across the sample was monitored to detect bismuth entry and breakthrough points.

Injection Test Results

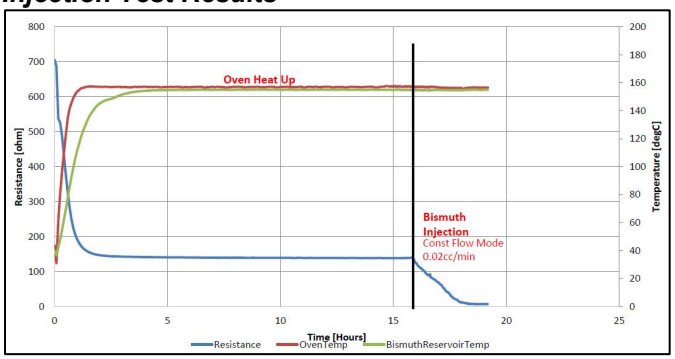

Figure 6: Resistance over time with bismuth injection at 0.02 mL/min.

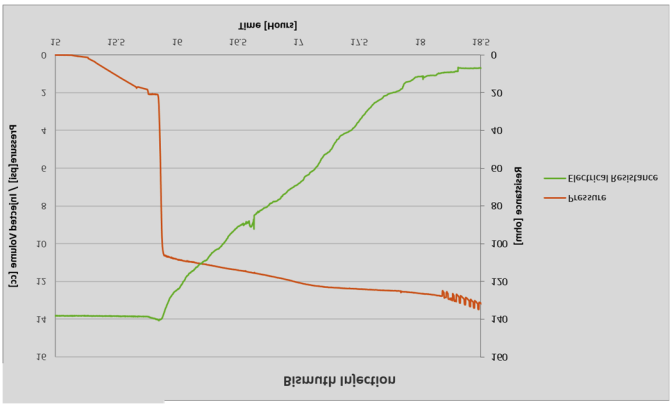

Figure 7: An upper saturation level of 35% Bismuth at breakthrough.

Figure 7, from entry to breakthrough, shows a total of 2.92 mL of bismuth was injected into the sample resulting in a 35.0% bismuth saturation. However, the pump continued to inject for a total of 3.96 mL yielding an upper saturation limit of 47.5%.

Discussion of Test Results

Typical results are shown in Figure 8. The static compressive strength test result shows that the compressive strength increases with the Bismuth influx into the rock matrix substantially while no significant difference could be observed for Young's Modulus or Poisson's Ratio.

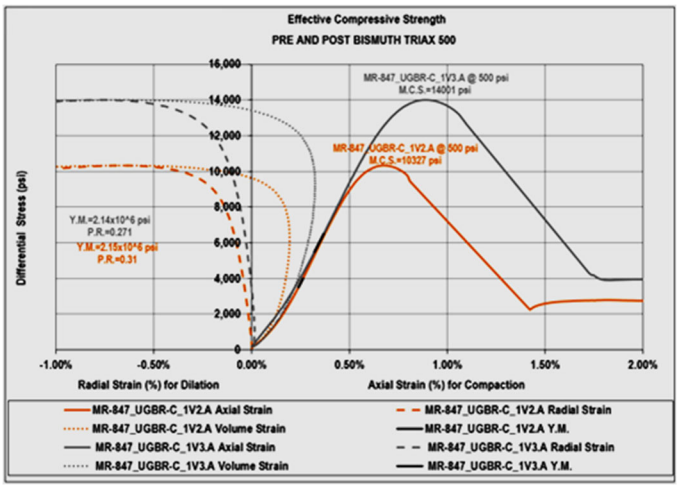

Figure 8: Compressive Strength Test Results.

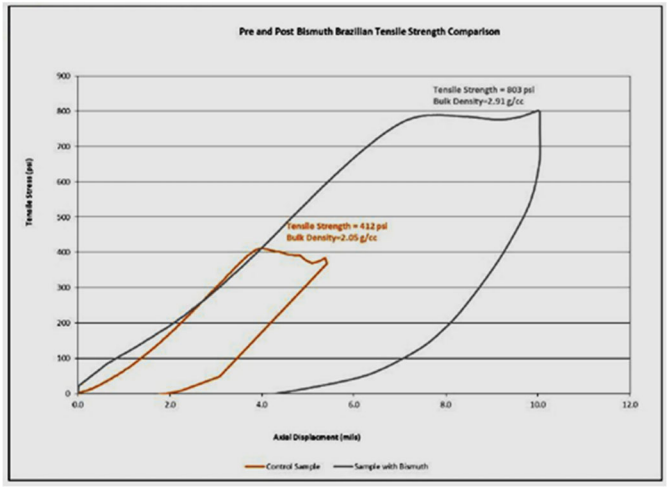

Figure 9: Brazilian Tensile Strength Test Results.

Figure 9 shows that the tensile strength is significantly increased because of the permeation of Bismuth-Tin into the formation. Table 4 gives the specific values are shown for several variables of the tested samples.

Table 4: Variables for Tested Sandstone Samples

	Porosity (%)	Permeability (mD)	Bismuth Saturation by Weight (%)	Compressive Strength (psi)	Tensile Strength (psi)	Poissons Ratio	Youngs Modulus
Base	22.2	328	0	10,327	412	0.31	1.83
Alloy	13.5	6.4	39.2	14,001	803	0.27	2.27

Table 5: Variables for Tested Carbonate Samples

	Porosity (%)	Permeability (mD)	Bismuth Saturation by Weight (%)	Compressive Strength (psi)	Tensile Strength (psi)	Poissons Ratio	Youngs Modulus
Base	15.8	348	0	6,003	419	0.21	3.12
Alloy	8.1	0.019	49.0	13,828	1,201	0.24	4.93

The highlighted line in Table 4 and Table 5 shows that with porosity influx into the matrix pore volume of the Alloy, porosity is reduced, compressive strength and tensile strength is increased, and permeability is reduced. The overall impact of altering these parameters is that the probability of fracking the formation resulting in lost circulation is significantly reduced if bismuth-tin alloy has permeated the formation.

Table 6: Fluid loss with and without Bismuth Metal Alloy

Step	Temperature (°F)	Bottom Valve	Time	MMO + BiSN 138, Cumulative filtrate (mL)	MMO (Blank), Cumulative filtrate (mL)
1	290	Shut	1 h	0	0
2	290	Open	5 sec	3	15
3	290 -> 150	Shut	~2 h, cooling	3	15
4	150	Open	30 min	5	> 50
5	150 -> 200	Shut	~1 h, heating	5	No control
6	200	Open	30 min	10	No control

Table 6 shows that the Mixed Metal Oxide fluid by itself had uncontrolled filtration while the one treated with the melted and cooled eutectic alloy created a seal within the disc matrix as per Figure 10 below.

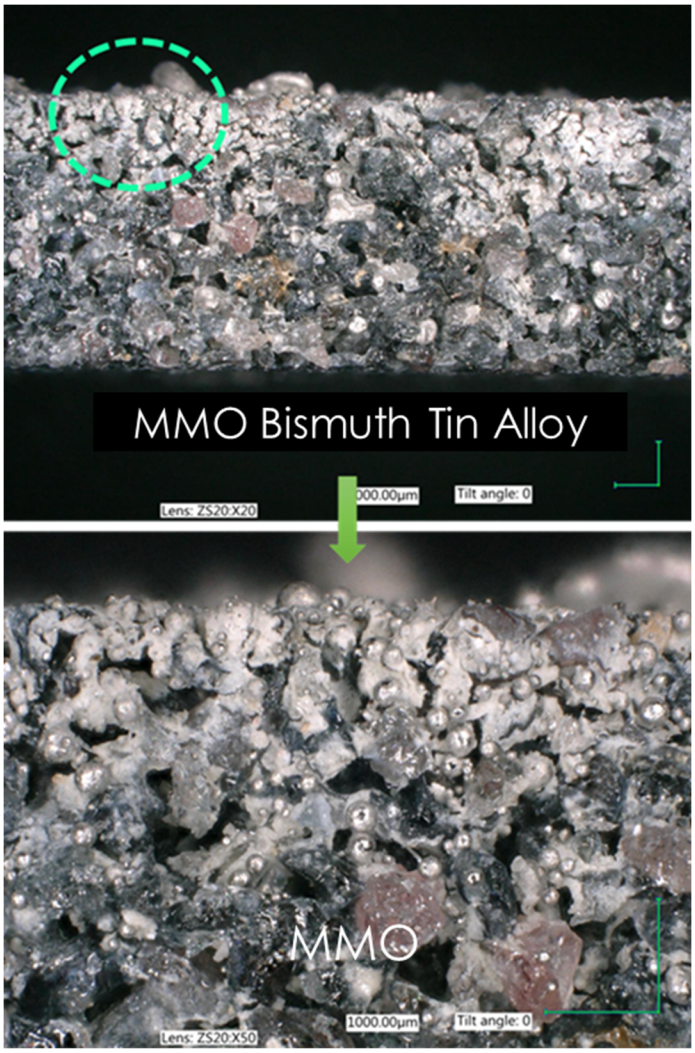

Figure 10: Scanning Electron Micrographs with and without eutectic metal alloy.

Conclusions

These results are not too surprising once we demonstrated that the alloy would penetrate the rock matrix. The experiment has been influx repeated demonstrating good relationships between the degree of alloy saturation and permeability, comprehensive and tensile strength. The implication for potential applications is large. Several companies have demonstrated various delivery systems for these types of materials. So, the logistics to apply the allow does exist. We begin with the idea of mitigating lost circulation, however this technology could be applied for the purpose of sealing a depleted/weakened zone for the purpose of extending a casing string. Also, in long cementing intervals the ability to seal gas zones might result in mitigating gas migration. Finally might improving the structural integrity of a rubble zone below a salt dome interface.

Acknowledgments

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