

# Materials science application in plug and abandonment of oil and gas wells

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## Abstract

The usage of material science has gained widespread attention in the petroleum industry in recent years, particularly in plug and abandonment (P&A) processes of oil and gas wells. Existing studies indicate that in P&A processes incorporation of new materials as a plug or barrier improves the plug properties such as strength, structure and durability. To fulfill the purpose of this paper, previous studies associated with the types of materials used in the P&A operations are reviewed. The study has revealed that the new materials can improve the performance of the plugs, ensuring adequate zonal isolation and extended well life. These findings highlight the potential use of material science in the petroleum industry.

## 1- Introduction

When an oil or gas well reaches the end of its lifetime, it must be plugged and abandoned permanently to avoid underground fluids leakages to the surrounding environment. The leakages may cause the contamination of groundwater as well as gas (methane) emission into the atmosphere increasing global warming, while the leakages in the case of offshore wells affect marine ecosystems. The plug and abandonment (P&A) operations usually consist of placing several plugs (such as cement slurry) in the wellbore to isolate the reservoir and other fluid-bearing formations [1]. Fig. 1 shows a typical method of P&A.

There are several paths of leakage in a plugged and abandoned well as depicted in Fig. 2. The leakages may go through the plug itself, depending on the permeability of the plug matrix or presence of internal cracks, or around the plug at the cement-casing interface, due to cracks creation during cement shrinkage or poor removal of drilling fluid. In some special wells, leakages may occur in the annulus outside the casing around the cement sheath at the cement-casing interface or at the cement-formation interface [2].

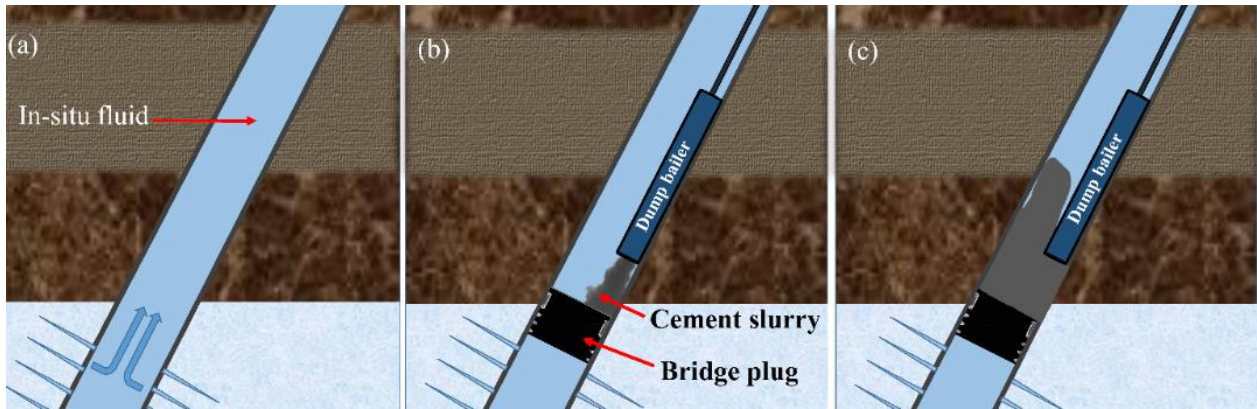


Figure 1. A sequence of schematic images of the cement plug placement in the P&A process: (a) initial well condition, typically full of in-situ fluid (drilling mud); (b) a bridge plug is placed, and a dump bailer injects the cement slurry on the bridge plug; and (c) the in-situ fluid is replaced by the cement slurry [1].

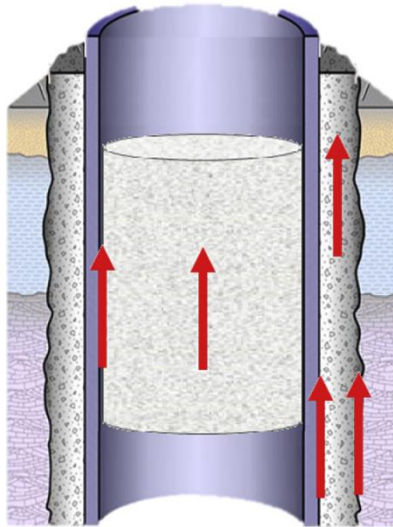


Figure 2. Schematic of potential leakage paths through or around the cement plug in an abandoned well [2].

Over time Portland cement has become the prime plugging material used for P&A because of low cost, user-friendly and commercial availability of Portland cement. However, researchers have searched for alternatives to Portland cement to improve properties relating to chemical shrinkage, thermal instability, long-term volume and chemical instability, cracking, durability in corrosive environments, low ductility, and degradation of properties due to contamination with other fluids such as drilling fluid.

Although Portland cement is by far the most commonly used plugging material, there are other types of alternative and emerging plugging materials that have been suggested such as thermosetting polymers, metals, and inorganic polymers (geopolymers) [3]. In this paper, a description of some of these materials is given, with an emphasis on Portland cement.

## 2- Plugging materials for P&A

The main functional characteristics of plugging materials are low permeability or impermeable, long-term durability at downhole conditions, non-shrinking, ductile or non-brittle, resistance to downhole fluids and gases, and sufficient bonding to casing and formation [4]. Any new plugging material designed for permanent P&A needs to be qualified before being applied in the field. The qualification process may be based on a systematic approach including experimental work and theoretical analysis. The qualification process includes preparation of the material and its placement, verification of its intended function when it is in place, and its durability at downhole conditions. Throughout time and with the development of material science, different types of plugging materials have been developed which are introduced in the following subsections.

### 2-1- Portland cement

The major components of Portland cement are  $\text{CaO}$ ,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Fe}_2\text{O}_3$ . When the cement is mixed with water and sufficiently over-saturated, some curing reactions occur and the mixture starts to form and build strength, i.e. the cement sets to become a solid material.

Portland cement is rarely used as neat cement without any additives, so a description of cement is incomplete without mentioning necessary additives. These include [5]:

- Retarder: is added to increase the setting time of cement to allow for longer pump times and/or the removal of the tubing used to place the cement.
- Accelerator: is used to decrease the setting time. These are used in wells to allow the cement to set up faster to avoid gas or fluid channelling, to prevent backflow in the tubing and when plugging the additive can shorten the wait time between plugs.
- Lost Circulation Material (LCM): is added to reduce the loss of cement to the formation before hardening.
- Weighting additives: are added to increase the density of cement to resist higher formation pressures. Materials such as barite and sand are used as weighting materials.
- Light weight additives: are added to reduce the cement density and thereby lessen the chances of losing cement to high-permeability or low fracture-gradient formations. Materials such as gel and foam are used to lighten cement slurry.
- Water loss additives: are added to reduce the water loss rate from the cement slurry. By reducing water loss before setting, the cement can harden properly and avoid premature drying which can decrease the strength of the cement.

These additives will affect both the short- and long-term properties of the placed cement volume.

The rheological behavior of the cement slurry depends on several factors including the water-cement ratio, size, and shape of cement grains, the chemical composition of the cement and the relative distribution of its components at the surface of cement grains, presence of additives, mixing and testing procedures. The concentration and shape of solid particles have also a significant effect on the rheological properties of the cement slurry. The yield stress and viscosity of cement slurry usually increase as the cement becomes fine, and also as the particle concentration increases. It has been observed that the flow of cement slurries show very complex rheological behavior. They have yield stress, they show shear-thinning and sometimes shear-thickening behavior, and they have time-dependent rheological properties. However, for practical oilfield purposes, cement slurries are invariably represented by time-independent models. Several shear stress-strain rate relationships have been developed for rheological properties of cement-based systems, among which the power-law (Eq. 1), Bingham (Eq. 2), and the Herschel-Bulkley (Eq. 3) models are the most commonly used in the well-cementing industry [6].

$$\tau = k\dot{\gamma}^n \quad (1)$$

$$\tau = \tau_0 + k\dot{\gamma} \quad (2)$$

$$\tau = \tau_0 + k\dot{\gamma}^n \quad (3)$$

Where  $\tau$ ,  $\tau_0$ ,  $\dot{\gamma}$ ,  $k$ ,  $n$  are shear stress, yield stress, shear rate, consistency index, and flow index, respectively. Additional complex three-parameter models have also been defined for predicting the behaviors of the cement slurries. These models combine both Newtonian and non-Newtonian features to define the behaviors of fluids properly (Table 1).

**Table 1. Some rheological models for cement slurry [7].**

<b>Flow models</b>	<b>Equation</b>
Casson	$\tau^{0.5} = \tau_0 + k\dot{\gamma}^{0.5}$ (4)
Sisko	$\tau = a(\dot{\gamma}) + b(\dot{\gamma}^n)$ (5)
Robertson–Stiff	$\tau = k(\tau_0 + \dot{\gamma})^n$ (6)

## 2-2- Thermosetting Polymers

Thermosetting materials, also known as thermoset polymers, are organic compounds which are characterized by their three-dimensional structures and low molecular weight (<10000 g/mol). Thermosetting polymers (resins) are particle-free fluids, which solidify into an impermeable material upon curing. The curing process is temperature-activated and occurs at a predefined temperature. In addition, viscosity and density can be tailored for various applications by the addition of particles. Thermosetting polymers are cross-linked to one another, Fig. 3, and due to the cross-links, these materials develop strength

[8]. The cross-links can break by heating or chemical interaction; however, to break these bonds the conditions need to be severe.

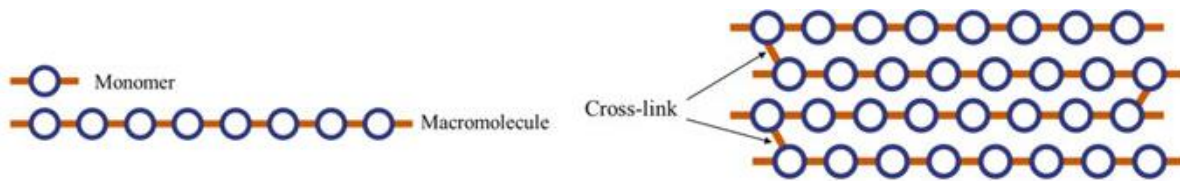


Figure 3. Structure of thermosetting polymers made of macromolecules and monomers [8].

The stability of thermosetting materials depends on the density of cross-links and aromatic content of the polymer. These materials are usually brittle in solid state and their brittleness is a function of polymer and curing pressure and temperature. They have also some other disadvantages such as interaction with brine and depolymerization, the issue regarding toxicity, deterioration in contact with a high-pH medium, and chemical shrinkage. On the other hand, there are some benefits in using these materials such as strong bond to formation and casing, proper mechanical properties, chemically inert to wellbore fluids and formations, low setting time, high tensile strength, and solid free (no grains).

### 2-3- Inorganic polymers

Inorganic polymers, broadly known as geopolymers, are a type of inorganic, rock-like materials that can be described as artificial stone. Owing to long chains and repeating units in the structure, they are polymers but having alkali-activated tetrahedral aluminosilicate minerals instead of carbon element, with the low calcium content. Geopolymers are based on different raw materials (i.e. precursor materials) such as fly ash, kaolinite and various types of rocks. By varying the type of raw material, different types of geopolymers with selected properties can be obtained. Properties such as low shrinkage, low permeability, strength development, stability at elevated temperatures, and tolerance to contamination with oil-based drilling fluids, suggest geopolymers to be an alternative to Portland cement for many oil well plugging applications (P&A). There are currently some unanswered questions regarding their usability, such as controlling pumpability while optimizing waiting on the setting. In addition, self-healing properties of geopolymer solutions were observed which may be beneficial from a long-term perspective [9].

### 2-4- Metals

There are some types of metals with a low melting point which have been suggested as permanent plugging materials including metal Bismuth, Gallium, Antimony, or low-melt-point eutectic alloys (Cerro alloys) [3]. The most known eutectic alloy in the petroleum industry is bismuth-based alloy. Bismuth is brittle and a very weak radioactive material. Bismuth alloys have a melting point of 174 °F at ambient pressure. The bismuth-based alloys used in permanent P&A have very low permeability or are impermeable. These metals

are placed in the desired area through inexpensive operations. Controlling vertical heat propagation during the metal plug placement is arduous and the maximum length of the plug is limited. Also, these plugs are toxic if mercury or lead is used in the alloy.

### 2-5- Thermite

Recently, low melting point metals like thermite have been examined to permanently plug wells [10]. In this method, a thermite plug is burning slowly at the desired depth, which is an exothermic reaction that temperature rises dramatically. The reactants melt through the wellbore, including casing, cement and formation, and bond with the surrounding rock formation. After cooling, the result will be a solid and impermeable barrier that extends across the full cross-section of the well. This concept is a changing P&A technology if it works as intended. At present, the technology is still under development and is being tested and validated. A potential drawback and current concern are whether the rock around the formed plug is damaged; i.e., if any leak paths are created around the plug after cooling.

### 3- Conclusion

This review study focuses on the application of material science in the P&A operations of oil and gas wells. The study shows that the science of plugging materials has a high potential to enhance the efficiency of P&A operations to ensure adequate zonal isolation.

Based on the review made, studies show that a wide range of properties that make plugging material so useful, such physical and chemical characteristics, can also cause potential problems if the material is not properly used. Hence, further researches and studies are needed to improve and enhance the efficiency of plugging materials as well as clarify some environmental and health-related effects of them.

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