Enhanced Oil Recovery: An Innovative Approach to Optimize Liquid Hydrocarbon Recovery in a Depleted Reservoir*

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Search and Discovery Article #41068 (2012)*
Posted November 19, 2012

*Adapted from extended abstract prepared in conjunction with oral presentation at GEO-India, Greater Noida, New Delhi, India, January 12-14, 2011, AAPG©2012

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Abstract

Under an attractive reservoir pressure, reservoir fluids coexist as a mixture of liquid and gaseous hydrocarbon making it less viscous and more mobile through their onward migration from the deeper part of the reservoir overcoming the resistance offered by the forces like capillary pressure, surface tension, and heterogeneity to reach the exit with a high rate of recovery. Where as a depleted reservoir faces difficulties in recovery due to the separation of gaseous hydrocarbon from the parent fluid owing to drop in pressure and making it more viscous and less mobile to counter the resistance posed by overlying forces like capillary pressure and surface tension through its journey to the bore. Drop in pressure further enhances the problem by depositing finer particles in the migration path. To enhance the recovery factor in a depleted oil reservoir through an innovative method by exploiting the physical and chemical properties of reservoir water with that of alkaline earth metal resulting in to liberation of huge amount of gaseous Hydrogen in their reaction process. This will in turn help in clearing migration paths as well as enhancing oil recovery by decreasing the viscosity and increasing the mobility of the liquid hydrocarbon present in the reservoir.

Procedures and results

When a least reactive mixture of cold water and alkaline earth metal powder (magnesium) will be injected to the bottom part of the formation water (hot) layer underlying a liquid hydrocarbon layer with depleted pressure in a reservoir, the injected mixture will disperse through the hot water initiating an exothermic chemical reaction by liberating huge amount of gaseous hydrogen as well as excessive amount of heat.

The reaction is mild in cold water. When the magnesium metal is exposed to hot water or steam, the temperature of the metal increases and its inter-atomic bonds loosen (destabilize) making the magnesium atoms to give away their electrons more readily. The hydrogen atoms produced are not effectively adsorbed on the hot surface of the magnesium metal and the metal is continuously exposed to the attack of the hot water molecules.

Furthermore, in the hot water, the water molecules are more ionized (destabilized) giving more number of hydrogen ions to accept the electrons and more hydroxide ions to form the stable magnesium hydroxide. Hence, the reaction is vigorous in hot water and in steam. Another equally important reason for vigorous reaction in hot water is that the produced hydrogen gas is more thoroughly expelled from the layer of magnesium than in cold water due to the prevailing turbulence and as gases are generally less soluble under hot conditions in liquids.

$$Mg + 2H_2O = 2Mg(OH)_2 + H_2(g) + Heat(\Delta_f H^\circ = (-924.54 \text{ kJ/mol}))$$

In addition, magnesium reacts with all dilute mineral acids to produce hydrogen.

$$Mg + 2HCl = MgCl_2 + H_2(g) + Heat (\Delta_f H^{\circ} = -641.8 (kJ/mol))$$

 $Mg + H_2SO_4 = MgSO_4 + H_2(g)$

Through reaction processes, two products will be generated. The heavier part will settle down towards the bottom part of the reaction kitchen where as the lighter part i.e. gaseous hydrogen, will move upward through water layer to the overlying depleted liquid hydrocarbon layer. Owing to its high rate of miscibility the liquid hydrocarbon will be less viscous and more mobile only to accentuate its migration to the bore overcoming the resistances offered by the forces like capillary pressure and surface tension. Furthermore, the immiscible part of the liberated gas will move faster through oil zone ahead of the liquid hydrocarbon and in the process will clear the finer particles deposited in the migration paths deposited during the drop in reservoir pressure. This will further accentuate the migration process of liquid hydrocarbon to the bore enhancing the oil recovery factor. The whole reaction phenomena are visualized to be carried out in a reaction kitchen made by excessive circulations as illustrated in Figure 1.

As illustrated in Figure 2, a piece of porous and permeable core was taken and plugged to make a hole where a small amount of magnesium powder was placed inside. The core then was wrapped with a plastic sheet with a sealing agent on the top and bottom part of the plastic to expose only a small part on the top and bottom of the core and to seal the magnesium powder inside. The core piece then immersed in to the cold water placed in a beaker up to the hole containing magnesium powder. Slowly the chilled water percolated through the permeable pores of the core and comes in contact with the magnesium powder (verified after the experiment). After few minutes, a matchstick was lighted on the top of the core only to see no change in the normal phenomena. Then the beaker with chilled water and core was placed on a low flame of a Bunsen burner and allowed the water to raise its temperature slowly. At higher temperature the behavior of a lighted match stick on the top of the core was changed showing traces of liberated hydrogen gas. So also when the core piece of stage no 3 dipped in liquid hydrocarbon on the top and the the temperature of the chilled water was allowed to rise by placing the beaker on a Bunsen burner, miniscule of oil droplets were observed to be oozing out conforming the pushing action of liberated gaseous hydrogen below the oil film.

Other Salient Features Resulted through the Process

I. Hydrogen gas is highly miscible with the heavy oil present in the residual oil zone resulting in reducing the viscosity of heavy oil and enhancing its mobility further to reach the bore with ease (Figure 3).

$$Mg(s) + 2 H_2O(1) \rightarrow Mg(OH)_2(s) + H_2(g)$$

- II. Since the reaction is exothermic, through the reaction process, huge quantities of heat will be produced which will accentuate the vigor of the reaction producing more heat and the overlying liquid hydrocarbon will expand with the addition of heat giving rise to thermal expansion effect to it and helping in enhanced recovery as illustrated in Figure 4.
- III. Continuous rise in temperature will produce a huge amount of steam in the water layer, which will move upward to the overlying liquid hydrocarbon zone creating an extra effect of steam injection and will help in recovery enhancement as illustrated in Figure 5.
- IV. Clearance of obstructions hindering migration of fluid hydrocarbon in the migration path will increase the over all rate of injectivity of the formation for future operations.
- V. In the absence of formation water layer underlying the liquid hydrocarbon layer will not hinder the process because the mixture of cold water and alkaline metal injected to the formation below oil layer will take heat from the reservoir system only to continue the vigor of the reaction and to liberate gaseous hydrogen to do the rest.

Functional and Operational Part of the Model

This is an indigenous and innovative idea of the author expressed through a conceptual model and so far not tried in any part of the world to the best of his knowledge. Regarding the functional and operational part of the model is concerned, those can be worked out and some of the details are discussed below. As far as the quantity of hydrogen gas liberation from the above reactant (magnesium) which is of prime concern can be found out using the Ideal Gas Law shown by the equation PV=nRT, in which P represents the pressure in atmospheres, V represents the volume in liters, n represents the number of moles, R represents the constant 0.0823 L*Atm/mol*K, and T represents the temperature in degrees Kelvin.

It was found from a lab test that 0.47 g of magnesium with P=1.003 atm, $n = .00933 \text{ mol Mg} = [(.0933 \text{ mol MG*1H}_2)/1 \text{ mol Mg}] = .00933 \text{ mol H}_2$, R = 0.0823 L*Atm/mol*K and $T = 293.5^{\circ}$ K will liberate 0.2294 L of hydrogen gas. Liberation of the hydrogen gas from the reactants under subsurface conditions can be calculated with proper changes in pressure and temperature conditions.

Regarding the amount of reactants are to be injected will depend on the size and the depleted pressure of the reservoir in question as these factors will decide the volume of Hydrogen gas to be liberated and added to the overlying oil zone so as to increase its mobility. Once the approximate volume of gas required is calculated, the amount of reactants can also be worked out.

Regarding the quantum of heat generation, we have to consider the enthalpy change during the chemical reaction of Magnesium with hot water or acid. This is denoted by the sign ΔH° .

 ΔH (reaction) = energy of product - energy of reactants

In an exothermic reaction, the products have lecc energy than the reactants, so the ΔH will be negative. In case of magnesium, the ΔH is expressed in terms of energy, which can be converted to heat.

$$Mg + 2H_2O = 2Mg(OH)_2 + H_2(g) + Heat (\Delta_f H^\circ = (-924.54 \text{ kJ/mol}))$$

The amount of energy produced depends on the number of moles of the reactants. We cannot measure energy changes directly. What we measure is a temperature change, usually in a known volume of water. To convert temperature change into energy, the specific heat must be known. The specific heat of water, s, is $4.18 \text{ J g}^{-10}\text{C}^{-1}$. That means it takes 4.18 J of energy to heat one gram of water by 1°C. Diluted solutions such as acids are considered to have the same specific heat as water. By definition, 1.0 ml of water at room temperature has a mass of 1.0 g. So if magnesium ribbon reacts with 2.0 ml of dilute hydrochloric acid and raises its temperature by 12°C , then the energy released was energy change = mass*temperature change*specific heat = $2.0 \text{ g} * 12 \text{ OC} * 4.18 \text{ j g}^{-10}\text{C}^{-1} = 100 \text{ J}$. Therefore, the release of energy in case of exothermic reaction of Magnesium can hence be converted to heat.

Regarding the quantum of the steam generation, this will depend upon the initial temperature of the reservoir water, volume of water present, amount of the reactants used and the specific heat of the liquid present. As the energy released from the reactions will increase, the temperature of the reservoir water will again help in increasing the vigor of the reaction. So if we consider one gram of water in the reservoir at the initial temperature of 70° C will require $4.18 \text{ J} \times 30 = 125.4 \text{ J}$ of energy to reach 100° C then after the energy of latent heat of evaporation which is 2257 KJ/Kg will be required to convert that unit of water to steam. Therefore, the total steam production will be dependant on the release of amount of energy released by the enthalpy changes occurred in the reactants.

Since the additional recovery is dependant on all the above factors and this process has not been tried before in any part of the world, the only envisaged quantum of additional recovery of oil will be the mixed impact of liberated Hydrogen, thermal expansion effect and the steam injection effect.

Economic Analysis

The process has many positive economics.

- I. It is an alkaline earth metal and the eighth most abundant element in the Earth crust, where it constitutes about 2% by mass, so its availability is in plenty.
- II. The Mg²⁺ cation is the second most abundant cation in seawater (occurring at about 12% of the mass of sodium there), which makes seawater and sea-salt an attractive commercial source of Mg. To extract the magnesium, calcium hydroxide is added to seawater to form magnesium hydroxide precipitate.

$$MgCl_2 + Ca(OH)_2 \rightarrow Mg(OH)_2 + CaCl_2$$

Magnesium hydroxide (brucite) is insoluble in water so it can be filtered out, and reacted with hydrochloric acid to obtain concentrated magnesium chloride.

$$Mg(OH)_2 + 2 HCl \rightarrow MgCl_2 + 2 H_2O$$

From magnesium chloride, electrolysis produces magnesium. Magnesium can also be obtained by electrolysis of fused magnesium chloride from brines, wells, and seawater. At the cathode, the Mg²⁺ ion is reduced by two electrons to magnesium metal:

$$Mg^{2+} + 2 e^- \rightarrow Mg$$

At the anode, each pair of Cl⁻ ions is oxidized to chlorine gas, releasing two electrons to complete the circuit:

$$2 \text{ Cl}^- \rightarrow \text{Cl}_2(g) + 2 \text{ e}^-$$

III. This metal has low toxicity so can be used safely.

IV. The high Mg⁺⁺ content (8.5%) of sea water contrasts strongly with the low Mg⁺⁺ content of the oil field water (generally 2-5%) which shows magnesium can be added to reservoir water safely since it is in low concentration and a wide range is left before saturation.

V. The economics of the marginal reservoirs will be improved.

Conclusion

This is an "out of box" approach to clear the migration paths of the fluid hydrocarbon, to enhance the depleted pressure of the reservoir and the effects of exothermic reactions can add and aid in making the process as an effective tool for enhanced oil recovery.

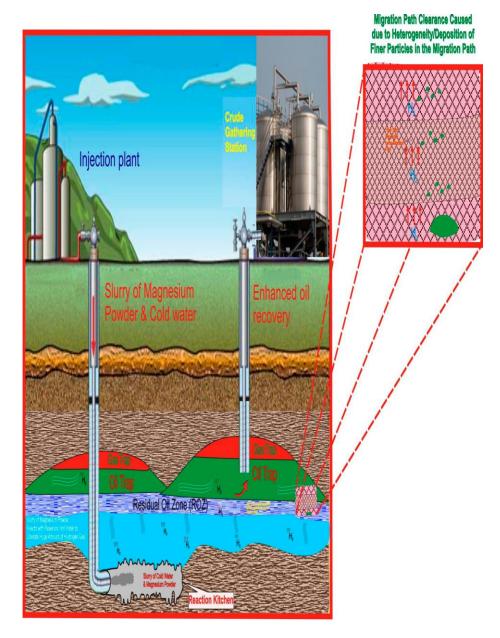


Figure 1. Conceptual model showing Reaction kitchen and Enhanced oil recovery.

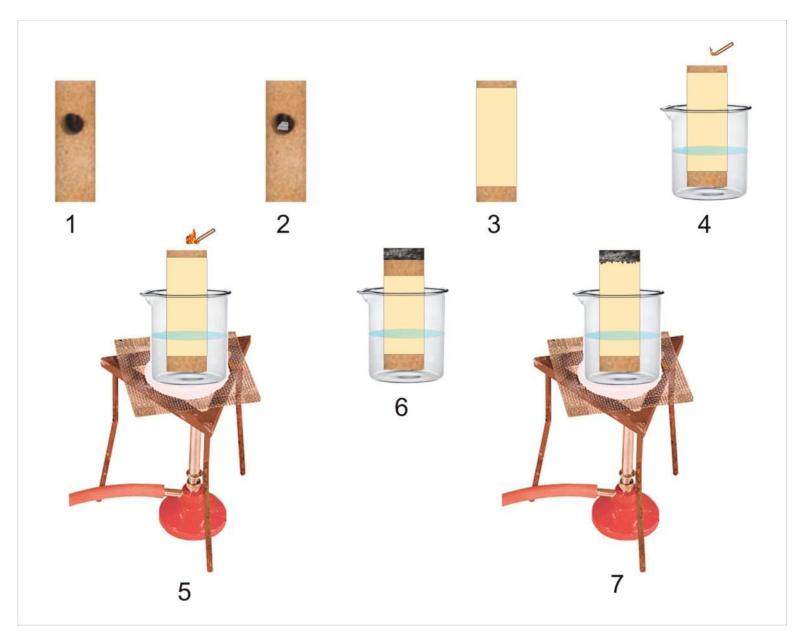


Figure 2. Phase wise experiments carried out on a porous and permeable piece of core in atmospheric temperature and pressure conditions.

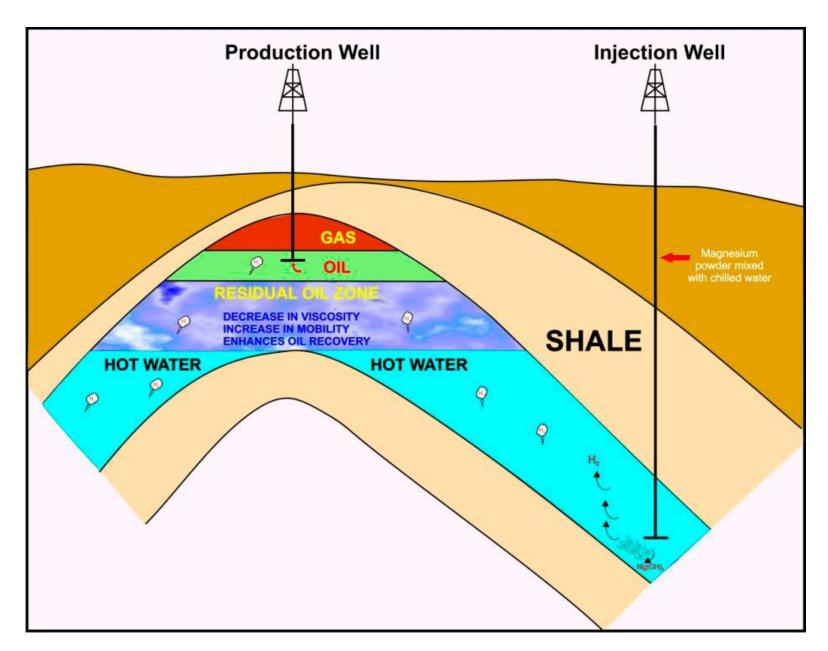


Figure 3. Liberated H₂ gas decreases the viscosity and increases the mobility of the heavy oil.

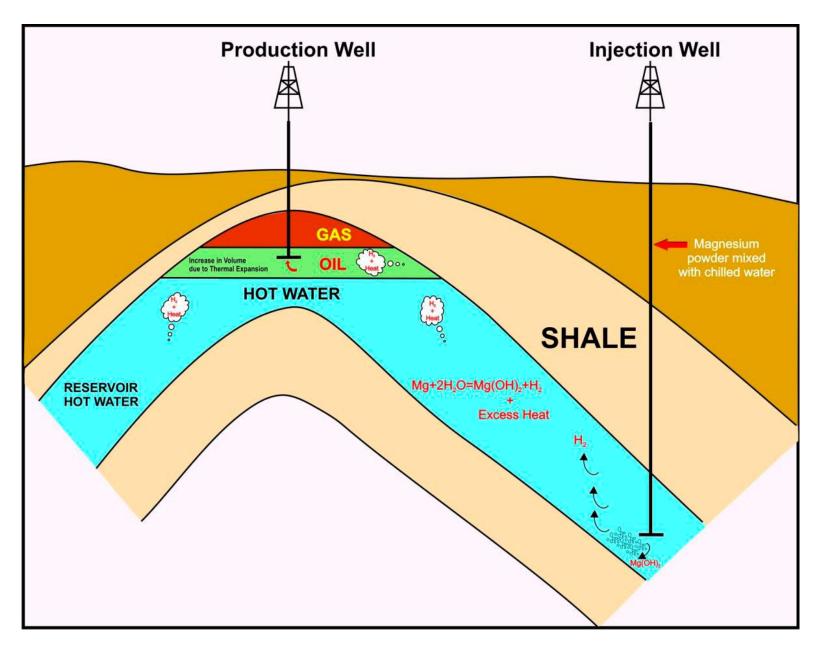


Figure 4. Exothermic reaction liberating huge amount of heat to give thermal expansion effect adding to EOR.

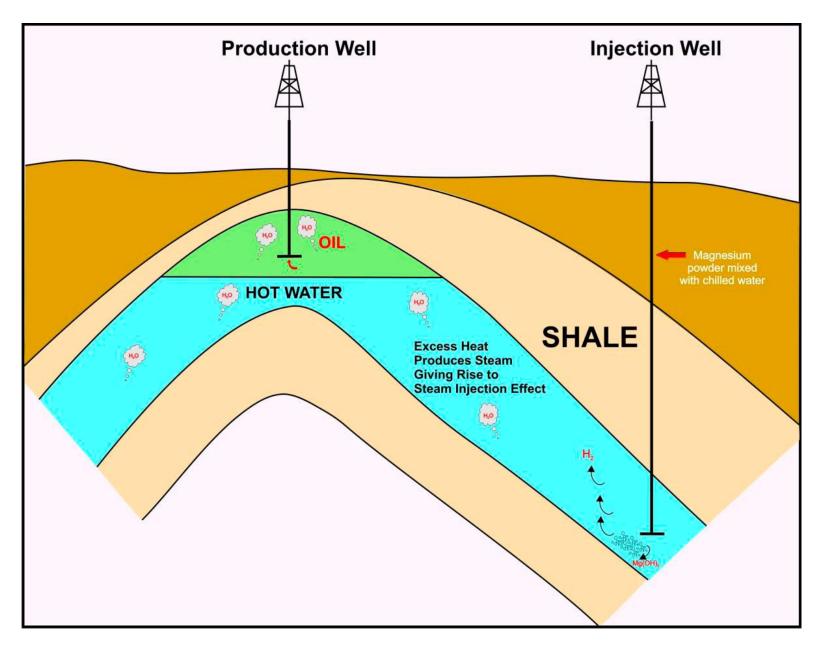


Figure 5. Huge amount of steam production gives rise to steam injection effect.