

Applications of tritium as a tracer in reservoir, drilling

by J. Bron, President

Bron & Associates, Calgary

TRITIUM IS A HYDROGEN isotope which contains one proton and two neutrons in the nucleus. The chemical symbol for tritium is ^3H or T. The other two hydrogen isotopes are protium (^1H), or ordinary hydrogen, and deuterium (^2H or D). Only the tritium nucleus is unstable or radioactive. The half-life of tritium ($T_{1/2}$) is 12.26 years. Because of its short half-life, tritium does not occur in formation water or any other source not in contact with the atmosphere. Tritium does occur in, for example, the atmosphere and surface water in extremely low quantities which are barely detectable.

The radioactivity of an element is unaffected by its chemical environment or any practical temperature. Hence, the tritium in tritiated methane (CH_3T) is exactly the same as in tritiated water (HTO). On decay, the tritium nucleus emits a low energy electron and changes into a stable helium-3 nucleus (^3He). The emitted electron can easily be stopped by an extremely thin material layer and, therefore, it has no penetrating power. No gamma rays are emitted during the nuclear decay.

Tritium is one of the safest radionuclei known and is widely used in industry for the dials of watches and other equipment. For this purpose, it is much safer than radium which was formerly used in the production of luminous dials. Since tritium can be incorporated into many compounds, its applications are numerous. In the petroleum industry, two important applications are found in reservoir tracing and drilling mud labeling.

Radioactive decay follows simple laws and a discussion of these laws may be useful to explain some of the terminology used in nuclear physics. Also, some of the results obtained can be used to answer some questions pertinent to the oil industry.

Given N radionuclei, the rate of disintegration is given by

$$(I) - dN/dt = kN$$

in which k is a rate constant and t is time. Equation (I) states that the rate of decay of the radionuclei is directly proportional to N, which implies that radioactivity can be expressed as a rate of decay or as the number N or the number of moles of the radiosubstance. For historical reasons the amount of a radiosubstance is expressed as

the rate of decay and is given in curies or becquerels. One curie (Ci) is 3.7×10^{10} (=K) becquerels (Bq). One Bq is one disintegration per second (dps). The Bq is a SI unit, but the Ci is most widely used on this continent. There are of course the standard diminutives such as the milli (m) and the micro (μ); hence mCi and μCi .

Integration of (I) between limits yields

$$(2) \ln(N_0/N_t) = kt$$

In (2), N_0 is the number of nuclei at time zero and N_t at time t. For practical reasons the constant k is customary removed and replaced by the half-life, $T_{1/2}$, which is the time required to reduce N to $1/2N$. The half-life is a measure of nuclear stability. Using (2) and the definition of $T_{1/2}$ it follows that

$$(3) \ln(N_0/N_t) = t(\ln 2)/T_{1/2}$$

Equation (3) can be used to correct for decay of a radiotracer during a certain application.

If there are C curies then (I) can be written after rearrangement and the introduction of the Avogadro number (M) as

$$(4) m = K.C. T_{1/2}/(M.\ln 2)$$

in which $m (= N/M)$ is the number of moles of the radiotracer. By means of (4) it can be calculated that 1 Ci of any tritiated substance, for which the half-life is 12.26 years, is 3.427×10^{-5} moles. For HTO one curie is less than 1 mg of material. In most applications the amount of tritiated radiotracer used does not exceed 50 Ci (eg. waterfloods). This small amount of tritiated water is a lot easier to handle than the large amount of chemical tracer needed for the same application.

The compounds HTO and CH_3T are isotopic molecules of ordinary water and methane respectively. Molecules differing only in isotopic substitution are very similar in their chemical and physical properties. Hence vapour pressure, solubility, density, boiling and melting points, and reactivity are practically the same for these substances. Because of its closeness to ordinary water, HTO is the ideal tracer for a waterflood, while tritiated hydrocarbons can be used to trace the corresponding compound in miscible flooding.

In drilling, labeling mud with HTO serves to evaluate the intrusion of mud water into the core and to aid the interpretation of DST results. For example the amount of HTO found in the core is directly proportional to the quantity of

water that entered the core during drilling. Similarly, in flooding the amount of tritiated tracer recovered is directly proportional to the amount of the corresponding injected fluid produced by a well.

For not always obvious reasons radiotracers have a somewhat higher success rate than chemical tracers. Also, as is the case in core analysis, radiosubstance may be much more readily and accurately determined than a chemical tracer. In other applications a carefully selected chemical tracer can be as useful or superior to a radiotracer. It must be emphasized that proper sampling is the key to the success of any tracer program.

Because of modern, sensitive instrumentation, tritiated compounds can be determined accurately at very low concentrations which are orders of magnitude smaller than the ones set by the most stringent safety standards. However, the injected amount of tracer is always such, that after dilution by the fluid to be traced, samples taken are always completely safe to handle without the need of any protection.

Safety is an important aspect of radiotracer applications. The injection can only be carried out by properly trained, experienced and licensed personnel and it is our experience that these injections are completely safe if proper attention is paid to details and well designed injection equipment is used.

As HTO is almost as volatile as ordinary water, the water vapour in equilibrium with the liquid phase will also contain HTO vapour. The maximum allowable concentration of HTO in air is only $2 \mu\text{Ci}/\text{m}^3$ and the question of how much of HTO will be in the vapour phase becomes important from the viewpoint of safety. The question to be answered is, given $Y \mu\text{Ci}/\text{m}^3$ of HTO in water, what is the amount of HTO in the air assuming equilibrium conditions.

A simple and useful expression for the amount of HTO in the air as a function of temperature can be derived by means of the ideal gas law, the above concepts and expressions, Raoult's law and the equation for the vapour pressure of "pure" HTO. The result is

$$(5) Q = (2.17 \times 10^{-6}/T) \cdot \exp(-5468/T + 26.31)$$

In (5), T is the thermodynamic temperature in degrees Kelvin and Q is the ratio of the concentration of HTO in air and the concentration of HTO in water. So Q is for example

$$(6) Q = (\mu\text{Ci}/\text{m}^3)_{\text{air}}/(\mu\text{Ci}/\text{m}^3)_{\text{water}}$$

Therefore, at 285K or 12C the concentration of HTO in air is about 100,000 times

lower than in the aqueous phase. Equation (5) is valid in the range of 273 to 333K.

In mud labeling a typical concentration of HTO is $1500 \mu\text{Ci}/\text{m}^3$ and the concentration of HTO in the air is then only $0.015 \mu\text{Ci}/\text{m}^3$ which is 133 times smaller than allowable concentration. In fact the usual equipment used to monitor for HTO in air cannot even detect such low concentrations. Also (5) gives an upper limit for HTO in air in this case, since dissolved salts and adequate ventilation will reduce the air concentration of HTO considerably. In the range of 0 to 15C, (5) can be written in a simpler, linear form:

$$(7) Q = (t + 8) 5 \times 10^{-7}$$

In (7), t is the temperature in degrees C.

In waterflooding the final concentration of HTO is usually much lower than $1500 \mu\text{Ci}/\text{m}^3$ and concentrations of 2 to $100 \mu\text{Ci}/\text{m}^3$ are typical. For biological and chemical reasons tritiated hydrogen and hydrocarbons are much less hazardous materials and can be used as gas tracers in very small quantities if the samples are burned to water and carbon dioxide. The tritium will then accumulate in the condensed

aqueous phase and therefore increase the sensitivity of detection greatly.

Because of low toxicity, low detection limits and versatility, tritium incorporated in various compounds is the most versatile and useful tracer for the oil industry.