NEW PERSPECTIVES IN THE INDUSTRIAL EXPLORATION FOR NATIVE HYDROGEN

Eric C. Gaucher[1]

DOI: 10.2138/gselements.16.1.8

Hydrogen gas (H_2), when combusted, produces heat and water. There is no pollution, just water vapor. When hydrogen combines with oxygen, there is no generation of carbon dioxide, no production of cyclic hydrocarbons, no sulfur oxides (SO_x), no nitrogen oxides (NO_x), no ozone cogeneration. It seems that hydrogen, along with efficient energy production, solves many of our pollution problems, from urban air pollution to global warming. In the so-called Hydrogen Age of the future (Holland and Provenzano 2007), H_2 will be mainly produced by the electrolysis of water using electricity that itself is derived from renewable energy sources or nuclear power plants. Steam methane reforming (a catalyzed reaction at high temperature where CH_4 is combined with water to produce CO_2 and H_2) will only be acceptable as a source of H_2 if it is associated with low-cost CO_2 storage. But, in this future energy landscape, what is the role of naturally occurring hydrogen, sometimes referred to as native hydrogen?

There has been a persistent idea in the petroleum industry that native hydrogen does not exist. This paradigm is clearly a response to the scarcity of H_2 in the millions of wells drilled for oil and natural gas in sedimentary basins. In 2002, Nigel J.P. Smith from the British Geological Survey claimed in the journal *First Break*, "It is time for explorationists to take hydrogen more seriously" (Smith 2002). Eighteen years later, things are moving in this direction. Academic research over the last three decades has begun to accumulate a significant number of observations of seeps of native hydrogen, together with abiotic methane (e.g., Smith et al. 2005; Etiope and Schoell 2014; Prinzhoffer and Deville 2015). Two main geological environments are involved: (1) Precambrian crystalline shields, (2) serpentinized ultramafic rocks at mid-ocean ridges and within land-based ophiolite-peridotite massifs. These two environments have only rarely been drilled by the oil and gas industry, explaining why significant reservoirs of hydrogen have had almost no chance of being fortuitously discovered during the exploration of petroleum provinces. The mining industry is frequently active in these kinds of environments but does not always monitor the composition of the gases that escape from the rocks. Furthermore, working depths in mining operations are generally less deep than in petroleum exploration, and the excavated rocks are probably already degassed due to blasting and other mining operations.

In many ways, the current state of exploration for native hydrogen resembles the beginnings of oil exploration. Before the pioneering work of "Colonel" Edwin Drake, whose famous oil strike in 1859 at Titusville (Pennsylvania, USA) set off the first oil rush, oil and gas were mainly known from seeps at the Earth's surface. Surface oil and gas seeps have been known since antiquity, for example in the Mesopotamian Area. The Bible even refers to Noah using bitumen for caulking and waterproofing during construction of the Ark, and methane escaping from the mud volcanoes of Azerbaijan were known to the Zoroastrian "fire-worshippers" more than 2,000 years ago. Drake invented "creekology", a petroleum prospecting method based on the systematic search for natural oil seeps that are typically found in erosion relief forms (i.e., valleys and creeks — hence the name). However, Drake had no knowledge of the anticline theory nor any idea of what creates a petroleum trap. It was only 26 years later in 1885 that American geologist Israel Charles White was the first to associate the existence of organic matter, the presence of reservoir rocks, and anticlinal traps with the successful location of oil and gas fields. The three key elements that constitute a petroleum system (source rock, reservoir, and trap) were finally connected.

1 Total E&P, R&D
Pau, France
E-mail: eric.gaucher@total.com

Geologists should now adopt the tripartite concept of "source rock, reservoir, and trap" in the exploration for native hydrogen and abiotic gases. Some important parts of the native hydrogen system are already known. Three main types of source rocks have already been identified: (1) ultrabasic rocks; (2) iron-rich cratons; (3) uranium-rich rocks. For the first two sources, the production of H_2 is linked to the oxidation of Fe(II) by H_2O. For the third source, the production of H_2 is attributable to the radiolysis of H_2O by natural radioactivity. The transformation of H_2 into abiotic CH_4 can occur under some circumstances through the Sabatier or Fischer–Tropsch reactions (Reeves and Fiebig 2020 this issue). This means that detection of abiotic methane may be a useful indicator for the presence of native hydrogen.

If we follow a discovery pathway analogous to that of the petroleum industry, the first method of exploration may be to find H_2 seeps in areas where source rocks are known. Seeps of native hydrogen and abiotic gases have already been localized in numerous places in subaerial settings. At least one of these seeps has been known since antiquity: Mount Chimaera (Yanartaş, Turkey), which is known for its "eternal fires". Ctesias is the oldest traceable author describing the phenomenon and is cited by Pliny the Elder in his second book of *Historia Naturalis* (77 AD). The gas at Mount Chimaera is a mixture of abiotic CH_4 (87 vol%) and H_2 (10 vol%) (Etiope et al. 2011). Etiope et al. (2011) estimate that 150–190 t of CH_4 is released to the atmosphere per year at this site. The seeps here have been continuously active for more than 2,000 years and, as suggested by Etiope et al. (2011), are evidently linked to low-temperature serpentinization processes (<100–150 °C) below the surface of Mount Chimaera. Numerous other abiotic gas seepages, most of which are associated with ophiolitic provinces, have been reported in the literature from locations around the world (including Turkey, Oman, Japan, Philippines, New Zealand, New Caledonia, Greece, Portugal, Spain, Italy, Bosnia, California, and Canada). In the mixed gas that is discharged at these localities, H_2 is generally less abundant than CH_4. Etiope et al. (2016 and references therein) report three sites of noticeable H_2-concentration (>2,600 ppm, or 0.26%, in the gas phase) in Ronda (Spain), Tablelands (Canada), and Happo (Japan). Monnin et al. (2014) indicate more than 20% H_2 from the Prony Bay seepage (New Caledonia). Boulart et al. (2013) report up to 12% H_2 in Oman's blue pools, and up to 1% H_2 in the hyperalkaline springs from the Voltry Massif (Italy).

Hydrogen seeps also have been observed in ancient cratons (including those in Russia, Brazil, USA, South Africa, and Finland) and, in some cases, form subcircular depressions that can emit significant quantities of H_2: 21,000–27,000 m^3 per day in one circular structure 1 km in diameter located in the Russian part of the European craton (Larin et al. 2015). The origin of H_2 in these latter cases remains unclear, but may be related to serpentinization of deeply buried ultrabasic rocks, radiolysis of water, or the oxidation of Fe(II)-bearing minerals (such as siderite, biotite, or amphibole).

Offshore (i.e., marine) production of H_2 and gas discharge in hydrothermal vents occur along mid-oceanic ridges, as demonstrated by pioneering discoveries on the East Pacific Ridge and the Mid-Atlantic Ridge (Welhan and Craig 1979; Charlou and Donval 1993; Bogdanov et al. 1995). One such case, the famous Lost City hydrothermal system, is not directly on the ridge but occurs close to the Atlantis Transform Fault, 15 km west from the Mid-Atlantic Ridge (Proskurowski et al. 2008). In many cases, serpentinization is the main reaction accounting for the elevated H_2 concentrations in the hydrothermal fluids.

Following the discoveries of oil and gas seeps, the "tipping point" for the petroleum industry was the well drilled by Colonel Drake. In the case of native hydrogen, we may be at this point (or close to it) with the recent discovery made in Mali near the village of Bourakebougou (Prinzhofer et al. 2018). After the first analysis of the well Bougou-1 confirmed the presence of almost pure hydrogen (98%), a dozen exploratory wells drilled in the vicinity confirmed the presence of a significant hydrogen field (>8 km in diameter) with overpressured fluids (water + H_2). A "native hydrogen kitchen" (a natural geochemical reactor) apparently exists here, although we don't yet know how it functions. Beneath the site, five stacked reservoir intervals are separated from one another by doleritic sills. A system of reservoirs and traps is consequently present, as described by Prinzhofer and colleagues. In Mali, therefore, a complete and significant "H_2 system" seems to be described for the first time, raising exciting questions. What are the volumes of H_2 in these reservoirs? What are the results of the production test of the wells? Is long-term exploitation feasible? Is this resource renewable? Can we artificially enhance the production? Is there a local market or an export market for this energy source? Answers to these questions are not currently available, but we can imagine that they will come soon.

It is worth mentioning that opportunities to detect deep hydrogen reservoirs based on measurements of H_2 in soils or aquifers close to Earth's surface appear to be severely limited for three reasons. First, the extremely small size of the H_2 molecule allows it to advect or diffuse very rapidly through near-surface environments into the atmosphere. Second, the high reactivity of H_2 with many oxidants (such as Fe-oxides, Mn-oxides, and nitrates) can rapidly destroy H_2 in oxidized near-surface environments. Third, numerous microorganisms are avid consumers of H_2 as a source of energy to support their metabolisms (Ménez 2020 this issue), and these organisms may deplete H_2 in shallow environments. On this latter point, a rich literature exists that shows the link between the development of life and the availability of H_2 at Earth's surface (Martin et al. 2008; Russell et al. 2010). All these adverse factors suggest that the most successful exploration efforts are likely to involve drilling to a depth where these near-surface processes will be excluded.

This article is a broad summary of the current state of knowledge concerning the potential exploration for native hydrogen across the globe. Native hydrogen has been identified in numerous source rocks in zones beyond sedimentary basins where petroleum companies typically operate. At the beginning of 2019 we may be at a tipping point with the first exploitable H_2 field, potentially discovered in Mali. Of course, a number of issues and questions must still be resolved if these initial discoveries are to be transformed into a sustainable and abundant source of energy for society. However, the competencies that exist in the petroleum industry can readily be adapted by and to this new sector. New expertise will be needed to account for the reactivity of the hydrogen molecule in order to maximize exploration efforts and minimize the potential for chemical or biological consumption.

Now is the time to launch R&D projects that couple geology, geophysics, geomechanics, hydrology, and geochemistry, together with deep exploration wells, in the search for exploitable native hydrogen. This objective is a 21st century challenge for any exploration company that has a pioneering spirit.

ACKNOWLEDGMENTS

Sylvain Calassou and many colleagues (TOTAL R&D) are thanked for fruitful discussions. The author also thanks the editors of *Elements* for their invitation to write this Perspective, which is his own personal vision.

REFERENCES

Bogdanov YA and 7 coauthors (1995) A study of the hydrothermal field at 14°45'N on the Mid-Atlantic Ridge using the MIR submersibles. BRIDGE Newsletter 9: 9-13

Boulart C and 5 coauthors (2013) Differences in gas venting from ultramafic-hosted warm springs: the example of Oman and Voltri ophiolites. Ofioliti 38: 143-156

Charlou J-L, Donval J-P (1993) Hydrothermal methane venting between 12°N and 26°N along the Mid-Atlantic Ridge. Journal of Geophysical Research: Solid Earth 98: 9625-9642

Etiope G, Schoell M, Hosgörmez H (2011) Abiotic methane flux from the Chimaera seep and Tekirova ophiolites (Turkey): understanding gas exhalation from low temperature serpentinization and implications for Mars. Earth and Planetary Science Letters 310: 96-104

Etiope G, Schoell M (2014) Abiotic gas: atypical but not rare. Elements 10: 291-296

Etiope G and 8 coauthors (2016) Abiotic methane seepage in the Ronda peridotite massif, southern Spain. Applied Geochemistry 66: 101-113

Holland G, Provenzano JJ (2007) The Hydrogen Age: Empowering a Clean-Energy Future. Gibbs M. Smith Inc., 384 pp

Larin N and 5 coauthors (2015) Natural molecular hydrogen seepage associated with surficial, rounded depressions on the European Craton in Russia. Natural Resources Research 24: 369-383

Martin W, Baross J, Kelley D, Russell MJ (2008) Hydrothermal vents and the origin of life. Nature Reviews Microbiology 6: 805-814

Ménez B (2020) Geologic hydrogen and methane as fuel for life. Elements 16: 39-46

Monnin C and 12 coauthors (2014) Fluid chemistry of the low temperature hyperalkaline hydrothermal system of Prony Bay (New Caledonia). Biogeosciences 11: 5687-5706

Prinzhofer A, Deville É (2015) Hydrogène naturel. La prochaine révolution énergétique? Une énergie inépuisable et non polluante. Belin, 190 pp

Prinzhofer A, Tahara Cissé CS, Diallo AB (2018) Discovery of a large accumulation of natural hydrogen in Bourakebougou (Mali). International Journal of Hydrogen Energy 43: 19315-19326

Proskurowski G and 7 coauthors (2008) Abiogenic hydrocarbon production at Lost City Hydrothermal Field. Science 319: 604-607

Reeves EP, Fiebig J (2020) Abiotic synthesis of methane and organic compounds in Earth's lithosphere. Elements 16: 25-32

Russell MJ, Hall AJ, Martin W (2010) Serpentinization as a source of energy at the origin of life. Geobiology 8: 355-371

Sherwood Lollar B, Onstott TC, Lacrampe-Couloume G, Ballentine CJ (2014) The contribution of the Precambrian continental lithosphere to global H_2 production. Nature 516: 379-382

Smith NJP (2002) It's time for explorationists to take hydrogen more seriously. First Break 20: 246-253

Smith NJP, Shepherd TJ, Styles MT, Williams GM (2005) Hydrogen exploration: a review of global hydrogen accumulations and implications for prospective areas in NW Europe. In: Doré AG, Vining BA (eds) Petrology Geology: North-West Europe and Global Perspectives – Proceedings of the 6th Petroleum Geology Conference. Geological Society, London. Petroleum Geology Conference Series 6: 349-358

Welhan JA, Craig H (1979) Methane and hydrogen in East Pacific Rise hydrothermal fluids. Geophysical Research Letters 6: 829-831

ABOUT THE AUTHOR

Eric C. Gaucher is an expert geochemist working in the petroleum industry. His work focuses on water–rock–gas interactions at the laboratory scale up to basin scale using experimental, field and numerical modeling methods. Although one of his main research objectives is to understand the behaviour of $CO_{2(g)}$ in sediments (e.g., diagenesis, CO_2 storage), he is now researching abiotic gases (H_2, CH_4) in natural systems mainly linked to serpentinization. Prior to coming to TOTAL in 2012, he was the head of a research unit at the French geological survey (BRGM) investigating the stability of clay formations for the management of nuclear waste. In 1993 he gained his MSc in Earth sciences from the École normale supérieure in Lyon (France) and in 1998 his PhD in geochemistry from the University of Paris VII.