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AVAILABILITY OF LARGE QUANTITIES OF LOW-DEUTERIUM HYDROGEN, AND POSSIBLE USES

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Abstract—Hydrogen produced electrolytically is isotopically light (depleted in deuterium) relative to the water in the electrolysis cell. Samples of the hydrogen by-product from two caustic soda/chlorine plants in New Zealand have been collected; one plant uses diaphragm cells and the other mercury cells. The hydrogen from one plant has been burnt to produce light water. These samples, commercial compressed hydrogen and Antarctic snow-melt (previously recommended as a source of light water) are approx 80, 50 and 35%, respectively, depleted in deuterium, relative to standard mean ocean water.

The water produced by burning hydrogen from the caustic/chlorine plants, could be available in tonnage quantities anywhere in the industrialised world. Work with this water has failed to confirm previous claims of accelerated germination of seeds and subsequent growth of plants, when using light water.

INTRODUCTION

WHILE planning a survey of groundwater movement in the aquifers of the Canterbury Plains, New Zealand, we investigated the possibility of using an isotopic tracer in the water. This would have avoided any suspicion of gain or loss of a chemical tracer, such as lithium ion, by interaction between the waters and soils or clays. However it appeared that the use of a commercially available isotopic tracer, such as deuterated water (D_2O), would be prohibitively expensive on the large scale required. One possibility that seemed worth pursuing, was to use water artifically depleted in deuterium (D), compared to the natural D abundance level rather than artificially enriched, and we discovered that low-deuterium water could readily be obtained in tonnage quantities from a common industrial chemical process. Although this approach was not eventually used for the ground water survey, we report here on the method of obtaining the low-deuterium water, and on our investigation of the germination of seeds in low-deuterium water.

ELECTROLYTIC PROCESSES INVOLVING HYDROGEN

It is well known that hydrogen produced electrolytically is isotopically light. The equilibrium separation factors can be achieved with care in a laboratory situation [1], but in large-scale cells the separation factor often deviates considerably from the equilibrium value.

Heavy-water production

The electrolysis of water has been used in the preparation of heavy water as the final process after preliminary concentration by fractional distillation. The water remaining in the cell becomes enriched in deuterium, because hydrogen is preferentially evolved.

Cylinder hydrogen

Hydrogen supplied as compressed gas by New Zealand Industrial Gases is produced by electrolysis of a caustic soda solution [2]. We have found this hydrogen to be considerably reduced in deuterium content when compared with the water with which the cell is fed.

Caustic/chlorine process

Chlorine is produced by electrolysis of a sodium chloride brine. Other products from the cell are sodium hydroxide (in solution) and hydrogen gas. There are two general types of cell in current use, known as the diaphragm cell and the mercury cell. The differences are outlined below. One installation of each type exists in New Zealand, and arrangements were made to collect hydrogen from each in order to determine the isotopic composition.

COLLECTION OF HYDROGEN FROM CAUSTIC/CHLORINE PLANTS, AND PRODUCTION OF WATER

Diaphragm cell

The Tasman Pulp and Paper Company operates an installation of 40 diaphragm cells at its mill at Kawerau. In these cells the cathode reaction is the reduction of water to hydroxide ions and hydrogen gas. The hydrogen emerges through a pipe in the cell cover, and is conveyed to a hydrogen manifold connecting all the cells. In this plant the hydrogen is simply discharged above the roof.

Hydrogen samples were obtained from individual cells by temporarily disconnecting the rubber hose leading to the hydrogen manifold, and re-connecting it to a pre-evacuated glass gas sampling bottle. The hydrogen thus collected was wet.

A sample of the water feed to the cells was also obtained.

Mercury cell

New Zealand Forest Products Ltd. operates a battery of mercury cells at its mill in Kinleith. Mercury cells have not been favoured for recent caustic/chlorine installations because of the pollution difficulties. In these cells the cathode is a horizontal pool of mercury. The overvoltage for hydrogen discharge on a mercury electrode is high, and so the cathode reaction here is the reduction of sodium ions to sodium amalgam in the cathode. The pool of mercury (containing sodium) flows continuously across the floor of the cell, and into another compartment known as the amalgam decomposer. Here the mercury flows counter-current to a stream of fresh water, which reacts with the amalgamated sodium to produce sodium hydroxide solution and hydrogen gas.

At this plant there was no convenient place to take a sample of hydrogen from any individual cell, and so samples were taken from the bulk compressed hydrogen store. This hydrogen was the mixed production of all the cells, which had been dried with sulphuric acid before compression.

A sample of the water used to supply the decomposers was also collected.

Production of water from electrolytic hydrogen

The engineers of New Zeland Forest Products Ltd. agreed to produce a sample of water by burning the hydrogen from their mercury cells. This plant normally produces hydrochloric acid from about 10% of its hydrogen, by burning the hydrogen with chlorine. The pilot burner of the hydrogen/chlorine burner was used to burn hydrogen in air, and about 1 l. of water was collected by condensing the combustion products.

The total production rate of chlorine at this plant is such as to allow the production of 3 t d^{-1} of hydrogen.

ISOTOPIC COMPOSITION OF ELECTROLYTIC HYDROGEN

Table 1 gives the isotopic compositions we determined for four cylinders of hydrogen supplied by New Zealand Industrial Gases; the hydrogen from the two caustic/chlorine plants and the water made by burning the hydrogen from one of them; and the water used as the feed in each case. Also included is a sample of melted Antarctic snow, which has been recommended [3] as a source of low-deuterium water.

TABLE 1. Isotopic composition of hydrogen and water from various sources

	δD‰*	D/H (ppma)†
Commercial compressed hydrogen		
Cylinder 1	−497	78
Cylinder 2	−535	72
Cylinder 3	−398	94
Cylinder 4	−430	89
Feed water	− 44	149
Diaphragm cell		
Hydrogen	−871	20
Feed water	− 30	151
Mercury cell		
Hydrogen	−808	30
Water produced by burning hydrogen	−753	38
Feed water	− 30	151
Antarctic snow	−354	101

* $\delta D‰ = \left[\frac{(D/H)\text{ sample}}{(D/H)_{SMOW}} - 1\right] \times 1000.$

† ppma = parts per million atoms; based on $(D/H)_{SMOW}$ = 155.8 ppma; SMOW = standard mean ocean water [4].

It is clear that all the samples of electrolytic hydrogen are depleted in deuterium to a considerable extent, more than the Antarctic snow-melt; and the samples from the caustic/chlorine cells are depleted most of all. The lower degree of deuterium depletion in the commercial compressed hydrogen is presumably due to the fact that electrolysis is allowed to go virtually to completion in these cells [2].

POSSIBLE USE TO AID GERMINATION OF SEEDS

Gleason and Friedman [3] reported that oats may grow better in water depleted in deuterium and oxygen-18 (^{18}O). Oat seeds germinated in 4 d in jars containing melted glacial ice from the Antarctic [depleted by 40% in D with respect to standard mean ocean water (SMOW)] but needed 17 d in similar jars with distilled ocean water. Kashutin [5] had previously reported a doubling of yields in cucumbers, radishes and wheat, when irrigated with melted snow water (compared with ordinary water); also egg production from hens and weight increases in piglets supplied with melted snow were double those of controls.

These very large effects seem surprising, as previous work on seeds [6, 7] had indicated no significant deleterious effects on germination rates, until the D_2O, content of the water was greater than 20%. More recently, Boreiko and Krouse [8] found no increase in germination rates in waters slightly depleted in deuterium compared to natural waters. We have repeated the experiment of Gleason and Friedman [3] and extended them to waters greatly depleted in deuterium, without being able to reproduce their beneficial results.

In experiment 1, 10 seeds each of oats (*Avena sativa*) and perennial ryegrass (*Lolium perenne*) were sown into plastic pots containing washed beach sand that had been adjusted to 20% moisture content (oven dry basis) with either distilled tap water or melted Antarctic snow. In order to minimise evaporation and to prevent exchange of atmospheric water with that contained in the sand cultures, each pot was enclosed in a polythene bag and sealed with a rubber band. Water condensing on the inner surface of the polythene bag was collected and isotopically analysed for deuterium and oxygen-18. It was not significantly different from the water initially added.

TABLE 2. Effect of distilled water and melted Antarctic snow on germination and growth of oats and perennial ryegrass

Species	Water treatment	Days from sowing (experiment 1)						
		3	4	5	6	7	10	10
		Seedling emergence (%)				Plant height (mm)		Fresh wt harvested (g/pot)
Oats	Distilled water	50	95	100	100	89.6	130.9	1.55
	Antarctic water (32% depleted in D)	30	95	100	100	80.5	134.5	1.35
	LSD (5%)					10.9	6.6	0.44
Ryegrass	Distilled water	0	50	80	90	39.8	75.8	0.09
	Antarctic water (32% depleted in D)	10	70	90	90	49.5	83.7	0.12
	LSD (5%)*					6.0	9.0	0.032

* Least significant difference at the 5% level [10].

There were two replicates of each treatment and the pot cultures were placed in a glass house at temperatures between 18 and 28°C. Until emergence commenced, the sealed pots were shaded to reduce temperature buildup. Table 2 shows the results of experiment 1, as germination rates, subsequent growth rates and final harvest weight.

In experiment 2, using a similar technique, seeds of ryegrass were grown with either distilled water, melted Antarctic snow or water made from caustic/chlorine electrolytic hydrogen. The temperature in the glasshouse was between 15 and 24°C. Results are given in Table 3.

In experiment 1 (Table 2) there was no major difference in either plant species between distilled water and Antarctic water. Oats appeared marginally better in distilled water while ryegrass did slightly better in Antarctic water. However, after 10 d growth there was no significant difference

TABLE 3. Effect of distilled water, melted Antarctic snow and water made from electrolytic hydrogen on germination and growth of perennial ryegrass

	Days from sowing (experiment 2)						
	5	6	7	8	7	12	12
	Seedling emergence (%)				Plant height (mm)		Fresh wt harvested (g/pot)
Distilled water	69	81	81	88	42.2	81.2	0.17
Antarctic water (32% depleted in D)	69	88	94	94	43.7	79.6	0.18
Water made from electrolytic hydrogen (75% depleted in D)	69	75	75	89	41.8	79.5	0.16
LSD (5%)*					2.2	4.4	0.034

* Least significant difference at the 5% level [10].

in plant height or fresh weight. In experiment 2 (Table 3) there were no significant differences between all three waters. Ryegrass grew marginally better in Antarctic water than in distilled water, and slightly better in distilled water than in water from electrolytic hydrogen.

Germination of ryegrass in experiment 1 (mean temperature 23°C) was faster than in experiment 2 (mean temperature 20°C).

Normal germination time for oats and other cereals at 20°C is 3–4 d [9]; this agrees with the germination time reported for oats in Table 2 (about 4 d). In the experiments of Gleason and Friedman [3], oats apparently germinated normally in Antarctic water (4 d) but were abnormally delayed in distilled ocean water (17 d); it is possible that the latter may have contained an impurity which adversely affected germination.

SUMMARY

Water depleted in deuterium by about 80% can readily be obtained in tonnage quantities by burning the hydrogen produced by caustic/chlorine electrolytic cells, which are widely dispersed in the industrialised world. This is a much better source than the previously recommended Antarctic snow-melt, which is only about one-third depleted. Hydrogen gas in commercial cylinders in New Zealand is one-third to one-half depleted in deuterium.

This light water could possibly be used as a tracer to study water movements on a fairly large scale.

Light water is unlikely to assist the germination of seeds or subsequent growth.

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