

**APPLICATION OF NATURALLY OCCURRING ISOTOPES
AND ARTIFICIAL RADIOACTIVE TRACER FOR
MONITORING WATER FLOODING IN OIL FIELD**

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ABSTRACT

Water flooding is an important operation to enhance oil recovery. Water is injected in the oil formation under high pressure through an injection well. Movement of the injected water is needed to be traced to test the performance of water flood, investigate unexpected anomalies in flow and verify suspected geological barriers or flow channels, etc. In the present study environmental isotopes and artificial radiotracer (tritium) were used at Fimkassar Oil Field of Oil and Gas Development Company Limited (OGDCL) where water flooding was started in March 1996 in Sakessar Formation to maintain its pressure and enhance the oil recovery. Environmental isotopes: ^{18}O , ^2H & ^3H , and chloride contents were used to determine the breakthrough/transit time and contribution of fresh injected water. Water samples were collected from the injection well, production well and some other fields for reference indices of Sakessar Formation during June 1998 to August 1999. These samples were analyzed for the ^{18}O , ^2H & ^3H , and chloride contents. Results show that the water of production well is mixture of fresh water and formation water. The fresh water contribution varied from 67% to 80%, while remaining component was the old recharged formation water. This percentage did not change significantly from the time of break-through till the last sampling, which indicates good mixing in the reservoir and absence of any quick channel. The initial breakthrough time was 27 months as the fresh water contributed significantly in the first appearance of water in the production well in June 1998. Tritium tracer, which was injected in November 1998, appeared in the production well after 8 months. It shows that breakthrough time decreased with the passage of time. ^{14}C of inorganic carbon in the water present in Chorgali and Sakessar Formations was also analyzed which indicates that the water is at least few thousand years old.

APPLICATION OF NUCLEAR TECHNIQUES IN INTER- WELL TRACING FOR ENHANCED OIL RECOVERY

1. INTRODUCTION

Oil industry plays an important role in the economic development of a country. Efforts are made to get maximum oil recovery from a producing well as the drilling cost is very high and the success rate is low. When the formation pressure is dropped due to oil production, fluids are injected in the formation to maintain the formation pressure and push the oil towards producing well or sometimes pumping is done. Occasionally, the oil is produced by altering its properties to make it flow by injecting special materials/chemicals. The exploitation of oil by operations involving application of external energy or modifications of reservoir characteristics is most commonly termed as "enhanced oil recovery" (EOR). Water flooding and water based floods are widely used EOR methods. The principles of water flooding are described in many standard reservoir engineering texts and in special water flood monograph (Craig 1971; Wilhite, 1986). In this operation water is injected in the oil formation under high pressure through an injection well to enhance oil recovery of the well(s) of interest. In order to test the performance of water flood, the movement of injected water is needed to be traced which is called "interwell tracing".

Interwell (or alternatively, well-to-well) tracer testing is an increasingly used tool for reservoir characterization. Its usefulness stems from the fact that the test provides information concerning the flow of fluid on the reservoir scale (Trantham, 1980); Beer and Sheely, 1988). Tracers are powerful tool to: trace the movement of the injected fluid through the reservoir, monitor reservoir performance, investigate unexpected anomalies in flow, verify suspected geological barriers or flow channels, etc. (Zemel, 1995). Generally the injected fluid is labelled with tracer (radioactive or non-radioactive) and the produced fluid from the well(s) of interest is sampled and analyzed to determine the tracer response. The analysis of tracer response curve (concentration of tracer vs. time) can provide important information about the character of reservoir and makes it possible to improve production strategy. Such information can be used to evaluate flood performance, optimize the balance between injection and production rates, help to decide EOR

programmes, and improve the accuracy of the reservoir model.

Design and planning of the tracer programme is extremely important. It usually involves the choice of tracers, the amount of tracer, tracer injection, the sampling programme and interpretation of results. The “ideality” of tracers refers mainly to the chemical and physical behaviour of the tracer, which should have the following properties.

It should move at a velocity very close to the velocity of injected fluid and it should not be sorbed onto the geological material or react with the reservoir fluid.

- The tracer must have good chemical and thermal stability and should not be degradable by bacteria.
- The detection limit should, in general, be as low as possible in order to minimize the amount of tracer needed.
- The tracer should be of low toxicity to allow safe usage.
- The availability and cost of the tracer and the cost of analysis should be reasonable.

A variety of materials were used as water tracer in early work on streams, underground caverns, groundwater, and oilfields. Radioactive tracers have probably been the most used tracers in interwell tests during the last fifty years (e.g. Watkins and Mardch, 1954; Watkins et al., 1957; Watkins et al, 1962; Burwell, 1966; wheeler et al, 1985; Skilbrei et al., 1990; Lichtenberger, 1991). These radioactive tracers artificially made in nuclear reactors are the best tracers considering the above properties. As the oilfield tracer applications have roots in hydrology and groundwater studies, some of the environmental isotope tracers (naturally occurring isotopes) such as ^{18}O , ^2H and ^3H of water molecule, which are becoming popular for hydrological studies, can be used in interwell tracing. References about application of such tracers in oil field have not been encountered in literature, maybe due to involvement of sophisticated equipment like mass spectrometers. If sufficient analytical facilities for environmental isotopes are available such tracers can answer some of the important questions faced in water-flooding. They are the only means of distinguishing between injected water and formation water.

The present study was carried out at Fimkassar Oil Field of Oil and Gas Development Company Limited (OGDCL) for interwell tracing. Environmental isotopes:

deuterium (^2H), tritium (^3H) oxygen-18 (^{18}O), Carbon-13 (^{13}C), Carbon-14 (^{14}C) and artificial tritium were applied to investigate the movement of the water-flood from the injection well to the production well and dating of the formation water. The manuscript focuses on the application of environmental isotopes and artificial radioactive tracer to get the following information.

- Breakthrough of normal water-flood,
- Presence of any quick channel,
- Contribution of fresh water in the watercut,
- Transit time from injection well to production well in case of breakthrough of injected water,
- Recharge source and age of the Sakessar and Chorgali Formation water.

2. DESCRIPTION OF THE OILFIELD

The Fimkassar Oil Field is located in Potowar Basin, District Chakwal, Punjab. The site is about 2 km to the west of Dhudial Town, which is 75 km southwest of Islamabad. The field has two production wells (Well No. 1 and 2) and the third well (Well No. 3) is used as injection well for waterflooding. Well No. 1 is producing from Sakessar Formation while the Well No. 2 produces oil from Choregali Formation overlain by Sakessar Formation. Well No. 1 was put on regular production in October 1989 from Sakessar Formation. The daily production of oil fluctuated from 2500 barrels per day (bbl/day) to slightly over 4000 bbl/day up to mid 1992. Then it decreased gradually and reached about 2000 bbl/day at the end of 1995. In order to maintain the reservoir pressure in Sakessar Formation and enhance the production rate, water-flooding was started in March 1996 in the same formation. Rate of water injection was over 10,000 bbl/D in the beginning, which was lowered to about 6600 bbl/day in four steps and again raised to 7000 bbl/day. The injection pressure was 3000 psi upto April 1998 and then maintained at about 2500 psi. About six months after water-flooding, the oil production started increasing and reaching the maximum of about 3800 bbl/day during December 1997 to March 1999, it again declined at high rate. The well also started producing water with oil in June 1998. Afterward, the water-cut kept on increasing with the reduction in oil production. Up to June 2000 the daily oil production reduced to about 500 bbl/day, while

the water-cut approached to about 3000 bbl/day. The production rate of oil and water-cut have been shown by the histogram in Fig. 1. It shows that the change in gross production (oil and water) is not significant.

3. GEOLOGY

The geological structure along with the location of the wells at Fimkassar Oil Field is shown in Fig. 2 (reproduced from Integrated Reservoir Study, Fimkassar Field, OGDCL). The map shows that there are two major reverse faults which cut each other at about 90° . The structure is developed on Sakessar Formations along SW-NE direction, while the other fault is SE-NW. The throw of the fault shows that this structure was developed due to the compressional tectonics. The contours show that Well No. 1 is almost on the apex and encounters the Sakessar Formation at 2408 m subsea. Well No. 3 is 2.6 km almost to the west of Well No. 1 and encounters this formation at 2621 m subsea. However, according to the map it is below the oil-water contact. The Well No. 2 produces oil from Chorgali Formation, which overlies the Sakessar Formation and follows the same structure having the thickness about 50 m. This well is located about 800 m from Well No. 1 to the northeast direction towards the point of intersection of both the faults and it encounters the both Formations at 2356 m and 2424 m subsea respectively.

The term Sakessar Limestone was introduced by Gee (in Fermor, 1935) for the most prominent Eocene limestone unit in the Salt and Trans-Indus ranges. Sakessar Peak (lat. $32^\circ 31' N$; long. $71^\circ 56' E$) in the Salt Range has been designated the type locality. The formation is widely distributed in the Salt Range and the Surghar Range. It is about 100 m thick at Fimkassar. The unit consists dominantly of limestone with intercalations of shale. The shale is more prominent in the middle and bottom layers of the formation. The limestone, throughout its extent, is cream coloured to light gray, nodular, usually massive, with considerable development of chert in the upper part. The foraminifers indicate an Early Eocene age of the unit. Sakessar Formation is overlain by Chorgali Formation. Generally the formation has two parts. The lower part consists of shale and limestone, while the upper part is mainly limestone. The fauna indicates an Early Eocene age.

4. MATERIALS AND METHODS

4.1 Stable Isotopes

Environmental (naturally occurring) isotopes: ^{18}O (oxygen-18), ^2H (deuterium) and ^3H (tritium) were used as tracers to investigate hydraulic connection between the injection well and the production well. ^2H and ^{18}O are stable isotopes while ^3H is radioactive isotope. The isotopic abundance is different in precipitation on global basis. In Pakistan, there is wide temporal and spatial variation in isotopic signatures of precipitation. The isotopic fractionation takes place mainly during evaporation and condensation processes and its magnitude depends on various factors like temperature, seasonal, altitude, latitude, continental and amount effect (Quijano and Dray, 1983). Exchange of isotopes, mixing between different components and chemical reactions are also responsible for isotopic fractionation. Therefore, various sources of water have different isotope signatures which can be used as tracers. The isotope techniques are able to provide information which sometimes cannot be obtained with other techniques. These include: identification of hydraulic connection between different water bodies, their mixing characteristics, origin of water; determination of residence time/age of groundwater; etc.

The variations of the stable isotope ratios i.e. $^2\text{H}/^1\text{H}$ and $^{18}\text{O}/^{16}\text{O}$ in water samples are measured by a mass spectrometer and are expressed in terms of per mille difference ($\delta^2\text{H}\%$ or $\delta^{18}\text{O}\%$) with respect to the isotopic ratios of mean ocean water, which constitutes the reference standard V-SMOW (Vienna Standard Mean Ocean Water) (Gonfiantini, 1981).

$$\delta^2\text{H} \text{ or } \delta^{18}\text{O} (\%) = [(R_{\text{sample}} / R_{\text{V-SMOW}}) - 1] \times 1000 \quad (1)$$

Where, R is the isotopic ratio $^2\text{H}/^1\text{H}$ or $^{18}\text{O}/^{16}\text{O}$. The value of $R_{\text{V-SMOW}}$ is given as: $R(^{18}\text{O}/^{16}\text{O}) = (2005.2 \pm 0.45) \times 10^{-6}$ and $R(^2\text{H}/^1\text{H}) = (155.76 \pm 0.05) \times 10^{-6}$.

The $\delta^{18}\text{O}$ of water was measured by the CO_2 equilibration method (Sajjad, 1989). Water samples were reduced to hydrogen gas by zinc shots for $\delta^2\text{H}$ measurement (Coleman et al., 1982; Florkowski, 1985). Measurement uncertainties for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ are $\pm 0.1\%$ and $\pm 1.0\%$ respectively.

The dilution of ^{14}C through reaction is accounted for in the decay equation by the dilution factor or fraction, q and the above equation is modified to:

$$t = -8267 \cdot \ln \left[\frac{a_i^{14}\text{C}}{q \cdot a_0^{14}\text{C}} \right] \quad (6)$$

Unfortunately, the simplicity of this equation is deceiving. It is very difficult to calculate reasonably accurate value of the dilution factor, q . The development of carbonate and ^{13}C evolution in carbon cycle provides a basis for calculation of q . Some of the approaches to trace ^{14}C evolution and correct radiocarbon ages through using a tool kit of aqueous geochemistry, ^{13}C , and a spreadsheet program for modelling.

For ^{14}C analysis, total inorganic carbon of about 60 liter water samples is precipitated in the form of BaCO_3 in the field. After raising the pH of the water sample to about 11, BaCl_2 is added. Paerestol, a coagulation agent is used to collect the precipitate (Hussain, 1991). The samples are prepared in a vacuum system by conversion of the precipitate to CO_2 reacting with perchloric acid and direct absorption method of CO_2 in the mixture of commercial chemicals Carbosorb and Permafluor (scintillator). ^{14}C activity is determined by liquid scintillation counter (Qureshi et al., 1989).

5. RESULTS AND DISCUSSION

Isotopic data of the samples collected from the wells on regular basis and data of some other reference sources are given in Table 1. Isotopic value of Balkassar Oil Field and Turkwal Oil Well producing from Sakessar Formation are similar to that of water of Chorgali Formation. Hence, the isotope indices of Chorgali Formation (Well No. 2) can also be considered as the reference for water of Sakessar Formation. $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of fresh water injected in Well No. 3, (the additional source) have wide spread but these values are quite different from that of water in the formation. Similar is the case with tritium data i.e. both the sources are much different. So all these parameters provide information about their contribution in the production well. In the discussion below the water of formation and injected water are referred to as Well No. 2 and Well No. 3 respectively, and the produced water is referred to as Well No. 1.

Table 1. Monthly average isotopic data

Fimkassar Oil Field									
Month	Well # 3 (injection in Sakessar Formation)			Well # 2 (production from Chorgali Formation)			Well # 1 (production from Sakessar Formation)		
	$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)	TU	$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)	TU	$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)	TU
Jun-98	-3.6	-25.5	4.1	1.0	-77.7	0	-2.5	-41.6	5.2
Aug	-2.0	-7.1	11.6	1.5	-78.2	0	-2.0	-38.9	7.1
Sep	-2.3	-19.2		2.3	-83.7		-1.5	-38.5	4.9
Oct	-4.1	-29.6		2.2	-81.8		-2.2	-36.0	5.2
Nov	-3.9	-29.5	5.6	2.1	-82.9		-1.6	-38.8	5.4
Dec	-4.2	-30.6		2.0			-1.4	-41.4	4.5
Jan-99	-3.3	-29.8		2.3	-83.3		-2.2	-42.0	6.0
Feb	-3.6	-27.2		2.1	-81.4		-2.0	-37.3	
Mar	-2.8	-20.6		1.7	-79.1		-2.3	-36.6	
Apr	-3.1	-24.5		1.8	-79.8		-2.0	-35.0	
May	-3.0	-25.7		2.0	-78.5		-2.0	-32.4	
Jun	-2.7	-21.9		1.5	-79.7		-2.2	-34.2	
Jul	-2.7	-23.5		1.6	-78.7		-1.9	-33.4	
Aug	-3.6	-26.2		2.2	-78.3		-2.2	-33.8	
Turkwal Oil Field									
				2.64	-63.7	0			
Balkassar Oil Field									
				1.9	-76.5	0			

5.1 Temporal Variations

Tritium of Well No. 1 varies from 4 TU to 7 TU with the average value of 6 TU. It is totally absent in the formation water (Sakessar and Chorgali) indicating that it is older than at least 60 years (Truesdell and Hulston, 1980). Well No. 3 shows wide variation (i.e. 4 to 12 TU). Presence of tritium in Well No. 1 indicates mixing of fresh water with water of the formation (Clark and Fritz, 1998), otherwise its value would have been about zero TU. Natural tritium was found in the samples collected just after start of water appearance (June 1998) in this well. It means that the breakthrough was started at the same time. Well No. 2 having no tritium indicates that the Chorgali Formation does not have freshwater component at all.

Fig. 3 shows the temporal variation of $\delta^2\text{H}$ for all the three wells. Except first few samples, it is almost consistent (mostly around -80‰) for Well No. 2. The other two wells i.e. Well No. 3 used for injection and Well No. 1 (the production well) have small fluctuations. Well No. 3 shows little variation of $\delta^2\text{H}$ because its source is a surface stream, which reflects seasonal variation of isotopes and also due to isotope fractionation resulting from evaporation in surface ponds. The small variation in Well No. 1 might be

due to variation in $\delta^2\text{H}$ of the major source (Well No. 3) or minor change in contribution of fresh water. $\delta^2\text{H}$ of Well No. 1 never matched with that of Well No. 2, rather these values are more towards those of Well No. 3. It clearly shows that the water produced in Well No. 1 is mixture of both the sources with major contribution from the injection water. Apart from the first few data points, the distances of line representing the Well No. 1 from those of Well No. 2 & 3 do not change significantly. This evidence gives the idea that the contribution of fresh water and formation water in the production well is more or less uniform.

Variation of $\delta^{18}\text{O}$ of all the wells is also plotted in Fig. 4. Well No. 3 shows high fluctuations in $\delta^{18}\text{O}$ as compared to $\delta^2\text{H}$. Actually fractionation factor of $\delta^{18}\text{O}$ in evaporation/condensation is higher than $\delta^2\text{H}$ (Clark and Fritz, 1998) so $\delta^{18}\text{O}$ of the surface water being injected respond faster to changes in climatic parameters like temperature, humidity etc. The changes in $\delta^{18}\text{O}$ of Well No. 2 may be attributed to varying degree of ^{18}O shift due to exchange with different rocks/minerals (Giggenbach et al., 1983). Variations of $\delta^{18}\text{O}$ also confirm major contribution of Well No. 3 in the produced water of Well No. 1.

5.2 Frequency Distribution of $\delta^2\text{H}$

Frequency histogram of $\delta^2\text{H}$ for all the wells is shown in Fig. 5. $\delta^2\text{H}$ of Well No. 2 is distributed between -84‰ and -74‰ with mean value at -80‰ and modal class at -79‰. Well No. 3 has $\delta^2\text{H}$ from -30 to -18 ‰ with mean value at -24.4‰ (neglecting few out-lying data having very enriched values). $\delta^2\text{H}$ of Well No. 1 is distributed between -44‰ and -31‰ with modal class at -33‰ and mean value of -37‰. The following two component mixing model is used to determine the fractions of fresh water and formation water.

$$f_1 \delta_1 + f_2 \delta_2 = \delta_m \quad (7)$$

$$f_1 = \frac{\delta_m - \delta_2}{\delta_1 - \delta_2} \quad (8)$$

$$f_2 = 1 - f_1 \quad (9)$$

Where f_1 and f_2 are the fractions of fresh water and formation water. δ_1 , δ_2 and δ_m are $\delta^2\text{H}$ of fresh water, formation water and mixed water of production well respectively.

Using the mean values the contribution of fresh and formation water in the production water come out to be 77% and 23% respectively.

5.3 $\delta^{18}\text{O} - \delta^2\text{H}$ Diagram

$\delta^{18}\text{O}$ vs. $\delta^2\text{H}$ along with the local meteoric water line (LMWL) determined by Hussain et al. (1991) for nearby area (Sargodha) is plotted in Fig. 6. The data points pertaining to Well No. 2 lie in a group far below the LMWL, which also contains original reference point of Sakessar Formation water determined from Balkassar and Turkwal Fields. Although, its $\delta^{18}\text{O}$ ($\sim +2\%$) is like that of magmatic water and also connate water (water entrapped in the interstices of a sedimentary rock at the time the rock was deposited) but highly depleted values of $\delta^2\text{H}$ ($\sim -80\%$) rule out both the possibilities (Giggenbach, 1992). Such isotope indices show that the origin of this water is mainly meteoric water recharged from high altitude like the Northern Areas having original $\delta^{18}\text{O}$: $\sim -12\%$ and $\delta^2\text{H}$: $\sim -80\%$. Geology also supports this idea as these formations outcrop in northern areas. In this case, $\delta^{18}\text{O}$ of meteoric water might have shifted from -12% to $+2\%$ by exchanging with carbonate dominated rocks. Carbonate minerals are highly enriched in ^{18}O , with values close to $+29\%$. When the meteoric water comes in contact with such rocks, it undergoes high positive ^{18}O shift, especially the exchange process is faster at higher temperatures (Clark and Fritz, 1998). Hence the water present in the formation is not that water which the geological term “formation water” (connate water) means. Here the term “formation water” means the water present in the formation with out any contribution of fresh injected water. All the data points of Well No. 3 lie near the LMWL but scattered below. They are scattered because of various precipitation events having seasonal variations. Different magnitude of evaporation effect is also responsible for departure from the LMWL and scatter (Payne, 1983).

The data points pertaining to Well No. 1 are clustered on the mixing line of Well No. 2 and 3. It shows that the water produced from Well No. 1 is essentially the mixture of both the sources i.e., formation water and injected water. The contribution of fresh water calculated by two component mixing equation during June 1998 to August 1999, remains in the range from 67% to 80% that shows well mixing of both the components before discharging through the production well. It means the possibility of quick channel between the injection well and the production well is ruled out.

5.4 Chloride Data

Chemical concentrations in water are prone to changes due to dissolution/precipitation of minerals and chemical reactions. Chloride is relatively more conservative as compared to other ions, therefore it was also analysed to get some information about interconnection between the injection well and the production well. Seven sets of water samples collected from the wells of Fimkassar during February to August 1999 were analyzed for chloride contents (APHA, 1985). For reference value of the Sakessar formation water samples were also collected from different wells of Balkassar and Turkwal Oil Fields producing from the Sakessar formation and analyzed for their chloride contents. The ranges and mean values of chloride for Fimkassar wells and the individual values for the wells of other two fields are given in Table 2.

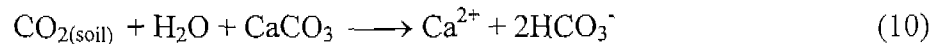
Table 2. Chloride contents of water samples of Fimkassar, Turkwal and Balkassar wells

Field	Well	Range of Cl (ppm)	Mean Cl (ppm)
Fimkassar Oil Field	Well No. 1 (Sakessar)	4328 - 4925	4640
	Well No. 2 (Chorgali)	2795 - 3186	3008
	Well No. 3 (Injected water)	82 - 155	110
Turkwal Oil Field	Well No. 1 (Sakessar)	12423 (May, 1999) 6340 (July, 2001)	9318
Balkassar Oil Field	P2 (Sakessar)	13723 (May, 1999) 25119 (July, 2001)	19421
	A3 (Sakessar)	5725 (May, 1999) 5148 (July, 2001)	5436
	A5 + A7 (Chorgali + Sakessar)	26189 (May, 1999)	26189

The data show that the Cl content of Sakessar Formation is very high as compared to that of Chorgali Formation. The chloride of water samples collected from Turkwal and Balkassar for reference value of water in Sakessar Formation has wide range i.e. 5148-25119 ppm. Even it shows large temporal variation in the samples collected from the same wells. Therefore, chloride seems unable to give information about the contribution of injected water.

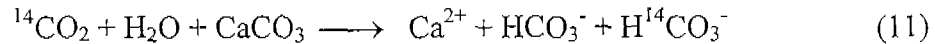
5.5 Dating of Formation Water

Absence of tritium in the water samples collected from Chorgali Formation and Sakessar Formation (Turkwal and Balkassar Oil Fields) shows that the water is older than sixty years because after five half-lives it reduced to about 0 TU (below detection limit). ^{14}C dating was done using some correction models. Chemical models could not be applied, as the required data of the recharge area is not available. In the approaches presented here, the diluting source of carbon is presumed to be ^{14}C -free. This is certainly the case with marine limestone, which is generally millions of years old.



Two sources of Dissolved Inorganic Carbon (DIC) then dominate in recharge environments - the ^{14}C -active component from the soil used to date the water, and a (generally) ^{14}C -free carbonate which dilutes $^{14}\text{C}_{(\text{soil})}$.

Under closed system conditions, the stoichiometry of calcite dissolution by carbonic acid imparts about a 50% dilution to the initial ^{14}C :



Under open system conditions, the DIC is continuously exchanging with the infinite reservoir of ^{14}C -active soil CO_2 . In this case, the initial ^{14}C activity of DIC ($a_0^{14}\text{C}_{\text{DIC}}$) remains unchanged at 100 percent modern carbon (pmC) or at the current initial ^{14}C activity. Unfortunately, the reality is somewhere in between. Most of the groundwaters reach calcite saturation during transition from open to closed conditions. The openness of the system and the contributions to the DIC pool can be reflected by the $\delta^{13}\text{C}$ of the DIC. Under fully closed conditions, the increase in $\delta^{13}\text{C}_{\text{DIC}}$ is due solely to mixing between DIC from soil ($\delta^{13}\text{C} \sim -12$ to -20‰) and marine carbonate ($\delta^{13}\text{C} \sim 0\text{‰}$). The closed system evolution of $\delta^{13}\text{C}_{\text{DIC}}$ is more dramatic because here the influence of calcite dissolution is felt. We can calculate ^{14}C dilution by the additional enrichment in $\delta^{13}\text{C}_{\text{DIC}}$ from this dilution.

(a) Statistical correction (STAT model)

Statistical models assume that after the initial carbon uptake in the soil zone by infiltrating water, some ^{14}C dilution will occur through the addition of ^{14}C -free carbon. On the basis of statistical evaluations to estimate an "initial" value for the ^{14}C activity, an

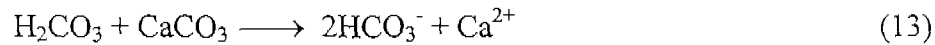
often quoted value is $q = 0.85$ (Vogel, 1970)

(b) Alkalinity correction (ALK model)

Where the recharge area cannot be studied, geochemical models are used that are based on the parameters measured in the water being dated. An often quoted approach is the Tamers (1975) or "chemical" correction based on initial and final carbonate (DIC) concentrations. It was proposed for groundwater in which calcite is dissolved under closed system conditions and is formulated as:

$$q_{ALK} = \frac{mH_2CO_3 + \frac{1}{2}mHCO_3^-}{mH_2CO_3 + mHCO_3^-} \quad (12)$$

For the vast majority of groundwaters this leads automatically to a q -factor of about 0.5 because of the reaction:



whereby most of the carbonic acid is consumed by limestone dissolution, and the original ^{14}C from soil carbon dioxide is diluted to about 50%.

(c) $\delta^{13}C$ mixing ($\delta^{13}C$ model)

Carbon-13 can be a good tracer of open and closed system evolution of DIC in groundwaters. The large difference in $\delta^{13}C$ between the soil-derived DIC and carbonate minerals in the aquifer can provide a reliable measure of ^{14}C dilution by carbonate dissolution. The $\delta^{13}C$ mixing model allows for incorporation of ^{14}C -active DIC during carbonate dissolution under open system conditions, and subsequent ^{14}C dilution under closed system conditions (Clark and Fritz, 1998). Pearson (1965) and Pearson and Hanshaw (1970) first introduced a $\delta^{13}C$ correction based on variations in ^{13}C abundances. Any process that adds, removes or exchanges carbon from the DIC pool and which thereby alters the ^{14}C concentrations will also affect the ^{13}C concentrations. The q -factor was obtained from a carbon isotope-mass balance.

$$q = \frac{\delta^{13}C_{DIC} - \delta^{13}C_{carb}}{\delta^{13}C_{soil} - \delta^{13}C_{carb}} \quad (14)$$

where:

$\delta^{13}C_{DIC}$ = measured ^{13}C in groundwater

$\delta^{13}C_{soil}$ = $\delta^{13}C$ of the soil CO_2 (usually close to -23‰)

$\delta^{13}\text{C}_{\text{carb}} = \delta^{13}\text{C}$ of the calcite being dissolved (usually close to 0‰)

$\delta^{13}\text{C}$ of soil CO_2 was determined in the possible recharge area and other parameters are taken as generally found in literature e.g. pH: 6.5, original ^{14}C activity: 100 pmC, partial pressure of soil CO_2 : 0.007, $\delta^{13}\text{C}$ of carbonate: 0 ‰.

Results of uncorrected, Statistical Correction Model (STAT), Alkalinity Correction Model (ALK) and $\delta^{13}\text{C}$ Mixing Model ($\delta^{13}\text{C}$) (Clark and Fritz, 1998) are given in Table 3.

Table 3. Results of ^{14}C dating by correction models

Formation	^{14}C (pmC)	$\delta^{13}\text{C}$ (‰)	$\delta^{13}\text{C}_{\text{soil}}$ (‰)	Groundwater age (years)			
				Uncorrected	STAT	ALK	$\delta^{13}\text{C}$
Sakessar	10.5	-2.5	-19	18632	17288	12901	3913
Chorgali	17.2	-3.8	-19	14552	13208	8821	3297

In the STAT and ALK Models, the dilutions of original ^{14}C activity are taken as 85% and 50% respectively which are not reliable. In the present case where the groundwater flows through limestone, after reaching the saturation point, processes of precipitation and re-dissolution keep on diluting the ^{14}C activity. In this case, $\delta^{13}\text{C}$ mixing model is the best to determine dilution factor and age of groundwater. Using this model, ages of groundwater in Sakessar and Chorgali Formations have been found to be 3913 years and 3297 years respectively. Uncertainties have not been calculated. Nevertheless, these ages can be considered as reasonable estimates. For hydrologists, the important information is that the formation water is few thousand years old.

5.6 Artificial Tritium Tracer Test

The water samples collected from Well No. 1 up to July 2001 were analysed for tritium. The results of artificial tritium tracer test (Table 4) show that the tracer took 240 days (8 months) to appear in the production well. It means that the break-through time of tracer was 8 months at later stage. While on the other hand, it took 27 months for the injected water to reach the production well at the initial stage. This difference in break-through time is mainly due to change in hydrodynamic properties of the reservoir. During the 31 months of water-flooding huge amount of water went into the formation. The oil

was pushed out to producing well and its place was occupied by water. As a result, the Tritium tracer took only 240 days (8 months) to reach the production well — hence a shorter break-through time. If the tracer had been injected at the start of flooding (March, 1996), its break-through time would have been similar (around 27 months) as indicated by stable isotopes.

Table 4: Tritium data of Well No. 1 (tracer injected on 06-11-1998)

Days (After injection)	Tritium (T.U)	Days (After injection)	Tritium (T.U)	Days (After injection)	Tritium (T.U)	Days (After injection)	Tritium (T.U)
8	5	282	597	674	8953	828	7971
15	6	289	637	681	9218	835	8502
51	4	415	5255	695	9427	842	8765
58	6	422	5807	702	9122	949	7700
72	6	429	5833	709	9431	856	8132
86	7	443	5916	716	9761	870	7215
99	9	450	6827	723	9729	877	7477
170	6	538	6353	730	7568	884	7360
184	12	548	9049	737	7390	891	7547
191	13	555	9037	744	8636	898	8038
198	11	562	9196	751	9561	905	7820
205	8	569	8976	758	9303	912	7511
212	9	576	8962	765	7489	919	7842
219	12	583	9159	772	9502	926	7530
233	37	611	9266	780	9572	933	7705
<u>240</u>	<u>70</u>	625	8907	786	9072	940	7584
247	121	632	8852	793	9044	947	7351
254	238	639	9106	800	8894	954	7343
261	262	646	9283	807	7783	961	7147
268	368	660	9499	814	8184	968	7828
275	459	667	9534	821	9205		

Tritium concentration in Well No. 1 plotted against the time elapsed after injection of the tracer (Fig. 7) gives the residence time distribution (RTD) of the tracer up to July 2001. Tritium concentration is still very high but the curve has started declining. Normally, a complete RTD gives information about the reservoir behaviour. This curve shows that the reservoir is generally well mixed and there are no preferential paths from the injection well to the production well. After the breakthrough in 8 months, the tracer reached to almost maximum concentration after about 18 months (548 days) and apparently, the decline started after 27 months (821 days). The broad peak indicates that the injected water sweeps a large volume.

6. CONCLUSIONS

The following conclusions were drawn.

- Well No. 1 (production well) has hydraulic connection with Well No. 3 (injection well). The water produced in Well No. 1 had 67% to 80% contribution of fresh injected water since the appearance of water in June 1998 to the last analysis of samples for environmental isotopes in August 1999.
- The initial breakthrough time was 27 months which was reduced to 8 months after November 1998.
- The reservoir is well mixed and there is no quick channel connecting the injection well and the production well. It seems that the injected water sweeps a large volume.
- Source of groundwater in these formations is meteoric water recharged from northern parts of the country and the residence time is few thousand years.

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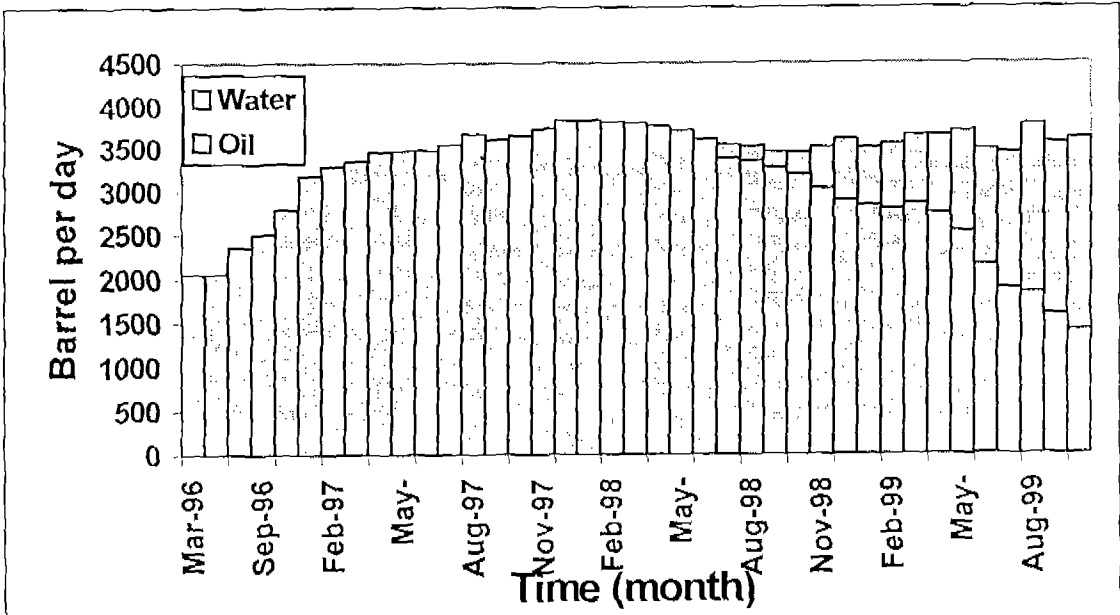


Fig. 1: Production rate of oil and water from well # 1

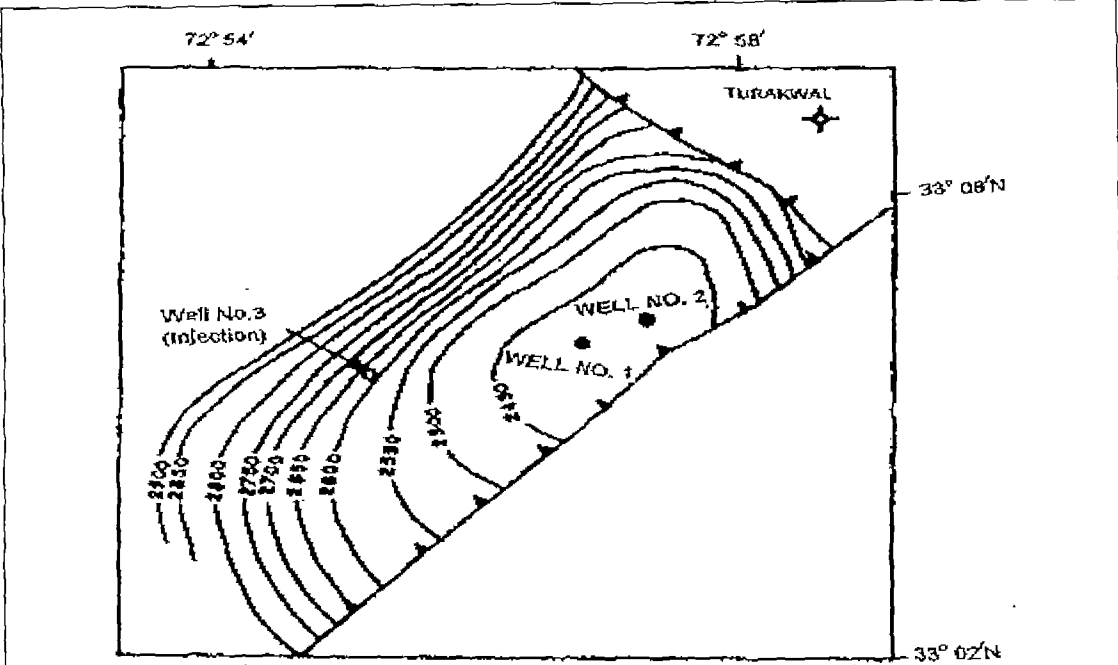


Fig. 2. Geological structure of Sakessar Formation at Fimkassar

Temporal variation of $\delta^2\text{H}$ of Well No. 1, 2 & 3

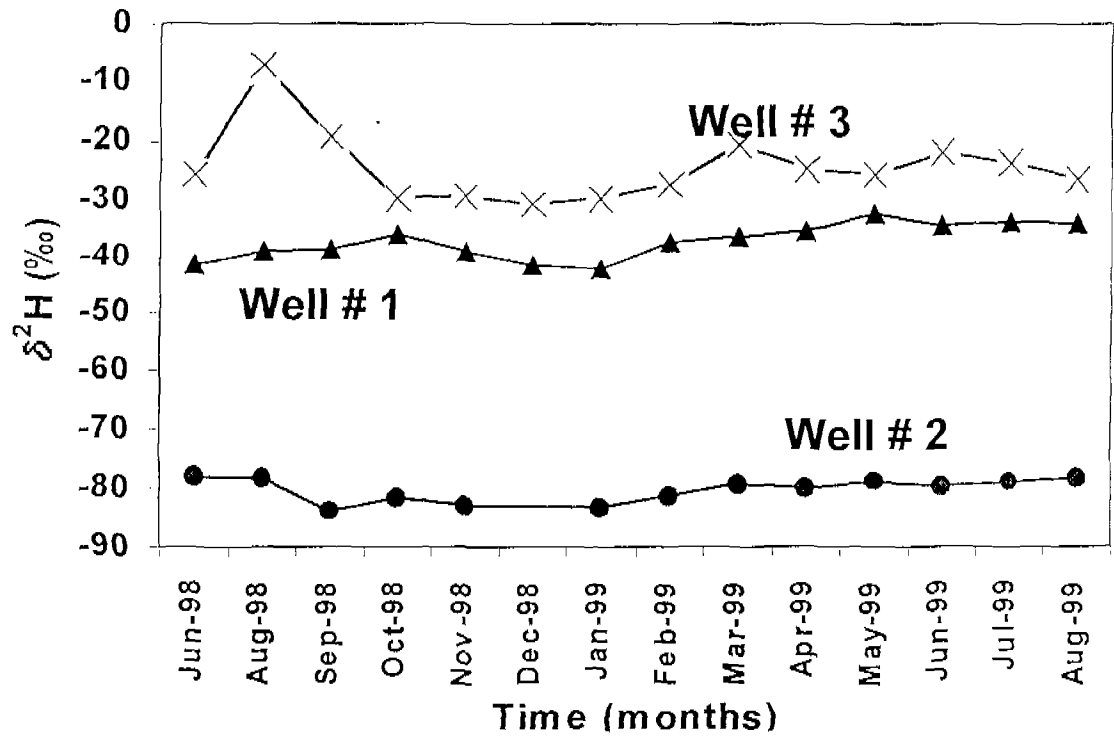


Fig. 3: Temporal variation of $\delta^2\text{H}$ of Well No. 1, 2 & 3.

Temporal Variation of $\delta^{18}\text{O}$ of Well No. 1, 2 & 3

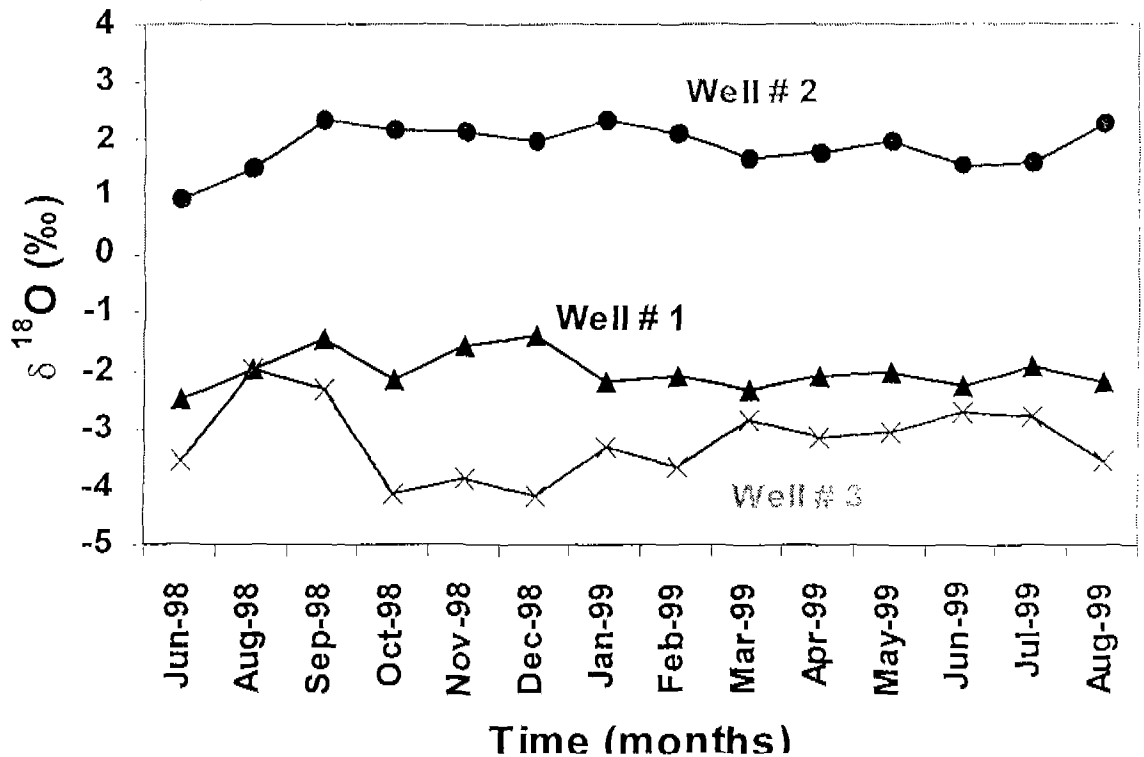


Fig. 4: Temporal variation of $\delta^{18}\text{O}$ of Well No. 1, 2 & 3.

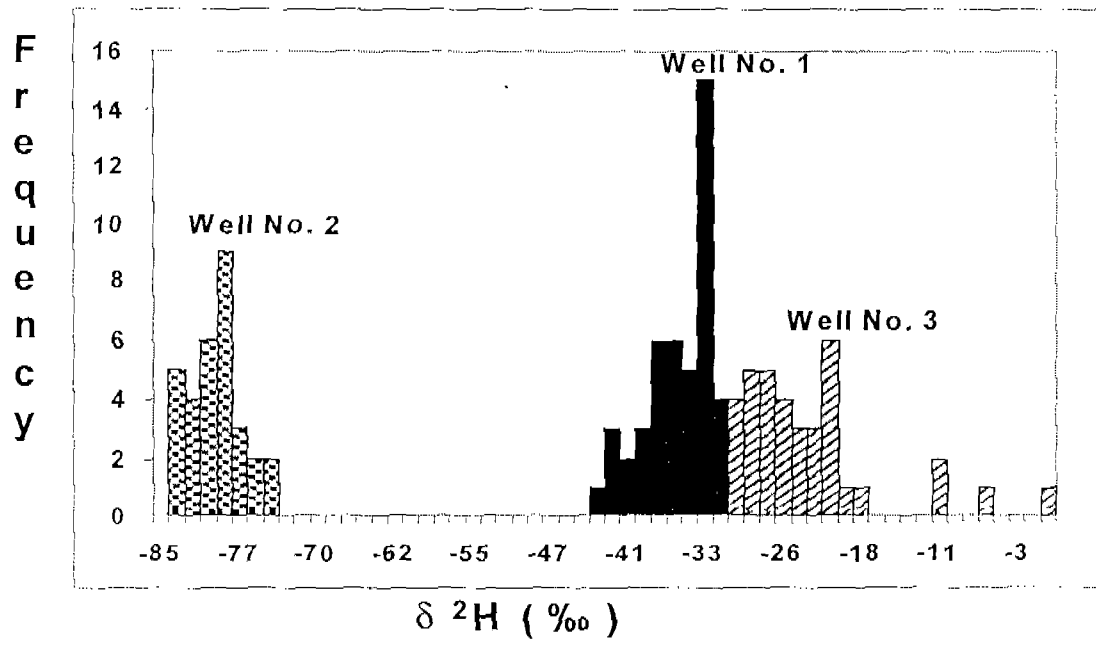


Fig. 5: Frequency histogram of $\delta^{2}\text{H}$ of well #

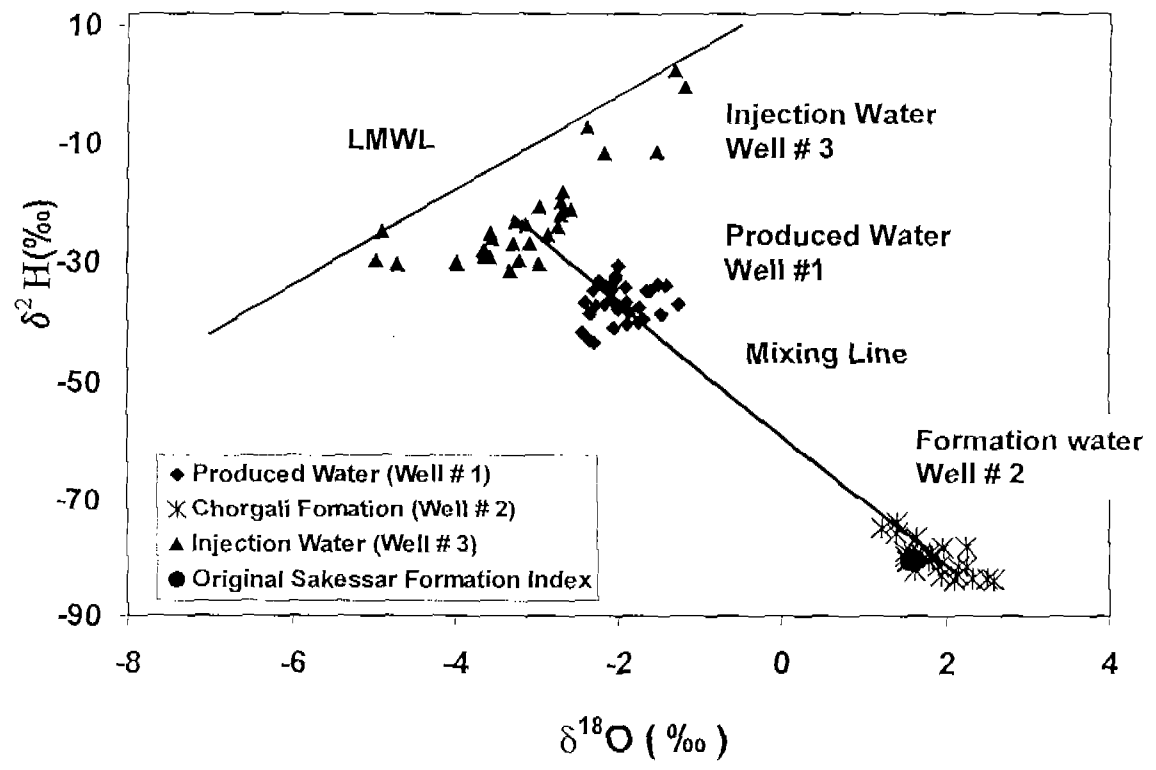


Fig. 6: Plot of $\delta^{18}\text{O}$ vs $\delta^{2}\text{H}$ of injected, produced & formation

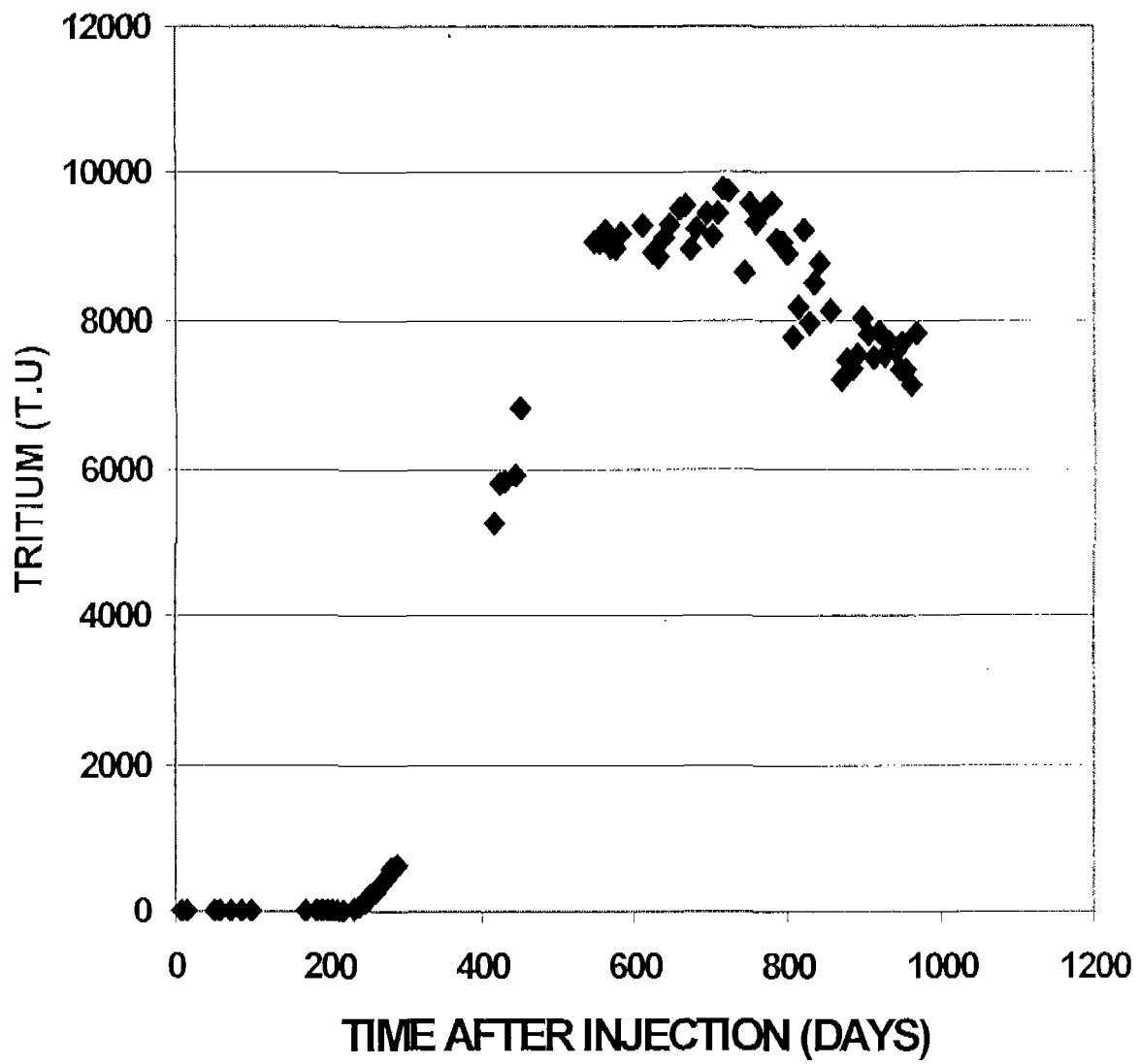


Fig. 7: TRACER RESPONSE VERSUS TIME AT WELL # 1