| Геол. ан. Балк. полуос.<br>Ann. Géol. Penins. Balk. | 64 (2001) | 233–241 | Београд, децембар 2002<br>Belgrade, Decembre 2002 |
|---|---|---|---|

UDC (УДК) 550.836:556.38(497.11)

Original scientific paper
Оригинални научни рад

# THE AGE OF GEOTHERMAL WATERS OF SERBIA AS AN INDICATOR OF CLIMATIC CHANGES

by

Mihailo Milivojević*

Climatic changes influence on surface water resources directly and in that way, more or less, more quickly or more slowly, by means of waterfalls, the quantity and quality of ground waters or hydrogeological resources, namely their sustenation. The conclusion about the influence of climatic changes on ground waters can be drawn on the basis of isotope research ($^{2}H$,$^{14}C$) by means of which their origin and age are determined most reliably. Present investigation results of the origin and age of ground water resources at the most famous hydrogeothermal regions, as well as the sustenance forecast of their quality and reserves depending on still existing and future climatic changes will be shown in this paper.

**Key words**: geothermal water, paleoclimate, age of water, isotope $^{14}C$, sustainable resource.

Климатске промене директно утичу на површинске водне ресурсе, а тиме, мање или више, од-носно брже или спорије, на количине и квалитет подземних или хидрогеолошких водних ресурса. О утицају климатских промена на подземне водне ресурсе може се закључивати директно и сигурно на основу изотопских испитивања помоћу којих се најпоузданије одређује порекло и старост подземних вода. У раду ће се изнети досадашњи резултати испитивања порекла и старости подземних водних ре-сурса са најпознатијих њихових налазишта и дати прогноза одрживости њиховог квалитета у зависности од већ насталих и будућих климатских промена.

**Кључне речи**: геотермална вода, палеоклима, старост воде, изотоп $^{14}C$, одрживост ресурса.

## INTRODUCTION

During two past decades we have witnessed unfavourable consequences of human activity on our environment, making this problem the common concern of the whole mankind. This self–destructive war, one has started against nature becomes more and more cruel and dramatic every day. One of its main causes is an amuck race for profit impacting our environment fatally. In other words, the conflict between profitable and ecological aims spreads constantly.

* Faculty of Mining and Geology, Institute of Hydrogeology, Geothermal Energy Laboratory, Djušina 7, 11 000 Belgrade (e-mail: martin@eunet.yu).

It is obvious that the shortage of water, food and raw materials, as well as pollution of atmosphere will be a big problem to the mankind in 21st century, bigger even than wars or political conflicts. It becomes clear to all people that "feast" of life resources will not last long. In connection with it, rich, namely scientifically and technologically most developed countries already get ready to solve the problem with regard to water in different ways. The solutions will most likely be in the form of conqueror wars against undeveloped countries having "water surplus" now. In this whole context hydrogeothermal resources as part of hydrogeological resources are of great significance because of their sustenation with regard to both quality and reserves in relation to other hydrogeological resources. Both results of the research of the age of the main geothermal waters occurrences (Fig. 1) from the reservoirs of hydrogeothermal convection systems on the territory of Serbia by Isotope methods performed within the evaluation of energetic potential of hydrogeothemal resources (Milivojević, 1989) and its significance for the evaluation of spa development sustenance are shown in this paper.

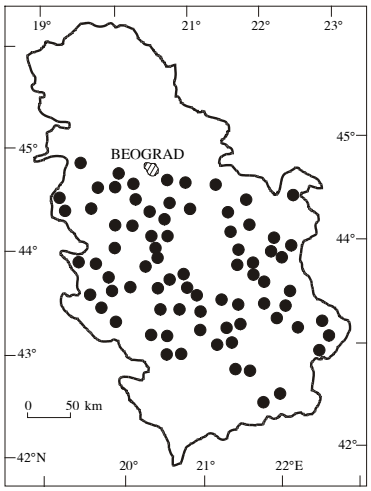


Fig. 1. The main geothermal waters occurrences in Serbia.
Сл. 1. Локације појава испитиваних геотермалних вода.

## THE AGE OF GEOTHERMAL WATERS AND CLIMATIC CHANGES

After defining isotope composition of rainfalls (Craig, 1961) isotope composition study of ground waters of all kinds started. It was established first that isotope composition of cold ground waters in aquifers at shallow depth in the earth's crust is approximately equivalent to the mean (average) isotope composition of the rainfalls, falling at the catchment area of aquifers. It can be said that since the discovery the conditions for the study of the influence of climatic changes on hydrogeological resources have been established. The influence of climatic changes on the regime of both rainfalls and hydrogeological resources can be discussed best on the basis of the age of ground waters The age of ground waters represents the period of time of their stay in an aquifer from the moment of atmospheric water infiltration into it to the moment of its outflow back to atmosphere.

Different radio active isotopes of elements in them are used for groundwater dating. Those are hydrogen, namely tritium T($^3$H), carbon $^{14}$C, silicon $^{32}$Si, chlorine $^{36}$Cl, argon $^{39}$Ar, krypton $^{81}$Kr, krypton $^{85}$Kr, or ratio U/He. The most appropriate, for dating, among these isotopes are tritium T ($^3$H) and carbon $^{14}$C. Tritium is an ideal marker of waters in general, because it goes into the composition of water molecules. Its wide spread in the atmosphere is well known and observed systematically. Restrictions owing to a short period of half decay are the only disadvantage in tritium application. Radioactive isotope of carbon $^{14}$C is the most convenient isotope for dating of ground waters for the only condition is that they contain dissolved bicarbonates and medium period of their retention in aquifers is several thousand years.

By measuring both specific activity of $^{14}$C and the content of T($^3$H) (tritium) it is established that all ground waters, according to their age, can be divided into four groups: 1) **Contemporary waters**. They have high specific activity $^{14}$C (>60% contemporary carbon) and tritium concentration equal, or a bit higher than annual average of tritium activity concentration in rainfalls. Surface waters and ground waters with relatively short period of retaining in the Earth's crust, namely in aquifers belong to this group. 2) **Holocene waters.** Meteoric waters infiltrated in aquifers during Holocene when the climate was warmer do not contain tritium and the specific activity of their $^{14}$C is 20% bigger than the specific activity of contemporary carbon, namely their age is about 10,000 years and denotes the end of the last glacial period; 3) **Waters from 10,000 to 25,000 years old**. The specific activity of $^{14}$C of these waters is from 5% to 20% of contemporary carbon, in other words they are from 10,000 to 25,000 years old and they do not contain tritium. 4) **Old waters**. The specific activity of $^{14}$C of the waters belonging to this group is 3% lower than the specific activity of contemporary carbon, in other words they are above 30,000 years old. They do not contain tritium either. As the upper limit of isotope $^{14}$C dating method is about 40,000 years considerably older waters belong to this group too.

## THE AGE OF GEOTHERMAL WATERS IN SERBIA

The isotope $^{14}$C dating method of ground waters includes both a number of the most famous mineral and geothermal water occurrences and a smaller number of shallow cold waters of Serbia region. The investigations were carried out in the period from 1986 to 1988 (Milivojević, 1989), and they represent the only investigations of this kind in Serbia so far. There were investigated totally 57 samples.

On the basis of the obtained results of investigations of the age of today's geothermal, mineral and cold shallow water phenomena from Serbia region it can be concluded that by using $^{14}$C it is possible to relate the water age to geological age, namely to younger periods of Quaternary. In connection with that it is interesting to see which climatic period today's ground waters date from, namely how much climatic changes influence the quality of ground water resources. As the isotope $^{14}$C enables dating to 40,000 years back the isotope content of water can be correlated reliably with climatic changes in Holocene.

In hydrogeothermal systems with relatively deep reservoirs, when interpreting underground water circulation conditions, it should be considered that climatic changes influence the processes of filling and emptying of the systems by mass, namely water. It is a general statement that glacial periods at higher latitudes and altitudes correlated with periods of low evaporation and high level of rainfalls at middle latitudes. Many research workers dealt with climatic change forecasts by means of air temperature changes in Quaternary, so several models were made. Long ago it was proved by different methods that during Quaternary climate often and considerably changed, so that glacial and warm periods replaced one another, in other words glacial and interglacial periods (Milanković, 1941). After the last glaciation climatic changes reduced considerably, they appeared in several last thousand years and have lasted till now.

For our considerations the most important models are those related to medium latitude of the Northern hemisphere. One of the oldest, and at the same time one among the best paleoclimatic models is the one performed by Ronjon & Viliams (1977) including the youngest period of Pleistocene and Holocene. According to their paleoclimatic reconstruction for the period of previous 40,000 to 20,000 years B.O. (before the origin) there were high rainfalls and a cold climate. In the period from 17,000 to 12,000 years B.O. intertropical aridity reigned, and then in the period from 11,000 to 5,000 years B.O. there were high rainfalls.

A lot of research workers dealt with climatic changes in Holocene because climatic changes in this youngest period of Quaternary are very important for understanding of climatic changes in historically past, present and future time. All those models published till 1983 were collected and reinterpreted by Vasseur & Lucazeau (1983). In their opinion, all models fit as far as the position and time of warm and cold periods are concerned on the basis of changes of paleotemperature. The results of their detailed analysis reach as far as 12,000 years back, starting from 1980, which was used as the time observation point, namely from this year climatic changes were reconstructed backward. They separated the following climatic periods: Subatlantic period (1000 to 2200 years) is generally considered to have been a little bit colder than today's period; Subboreal epoch (2200 to 5000 years) is considered as a warm one; Atlantic period (5000 to 7000 years) is the warmest in Holocene; Botnian period (7000 to 8000 years) is less warm than Atlantic period; Boreal period (8000 to 9500 years) is the one we are most familiar with, but in most models warmer than today's; Preboreal period (9500 to 10,500 years) matches the temperature increase of post Pleistocene glacial period. The last glaciation in West Europe (Würm) was between 10,500 and 65,000 years before the year 1980 (Woillard, 1979; Lamb, 1977; Washburn, 1980).

On the basis of the given results of paleoclimatic reconstructions it can be concluded that majority of artesian hydrogeological, namely hydrogeothermal systems were discarged intensively during cold climate in the period between 20,000 and 10,000 years B.O because rainfalls were low and catchment areas frozen and because of that water unpermeable and supplied when opposite climatic conditions prevailed, in other words in the period between 10,000 and 5,000 years B.O. Accordingly, important changes of artesian hydrogeological and hydrogeothermal systems took place in the period between 20,000 and 5,000 years B.O.

Climatic changes influence the content of stable isotopes in groundwaters. The general statement is that small contents of, $\delta^{18}O$ and $\delta^{2}H$ denote cold and wet paleoclimatic periods. In connection with this diagrams were made presenting the values of $\delta^{2}H$ and $\delta^{18}O$ in relation with the mentioned paleoclimatic classification, namely the age of water. One can see, on the Figs. 2 and 3, that reservoirs of more than a half of total number of investigated hydrogeothermal systems (about 60%) were reacharged in the period of 15,000 to 30,000 years ago when the climate was cold. Reservoirs of the remaining systems (about 40%) were recharged in the period from 2500 to 10,000 years ago, namely during the period of warm climate after the last glacial period.

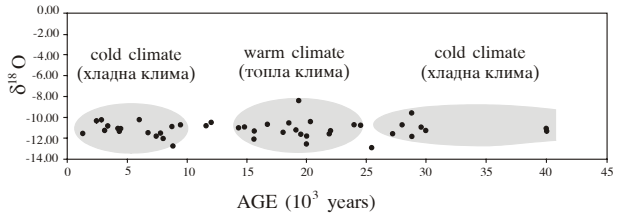


Fig. 2. Content of $\delta^{18}O$ versus age of geothermal water.
Сл. 2. Однос садржаја $\delta^{18}O$ и старости (према $^{14}C$) геотермалних вода.

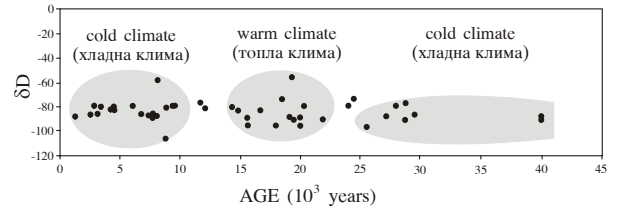


Fig. 3. Content of δD versus age of geothermal water.
Сл. 3. Однос садржаја δD и старости (према $^{14}C$) геотермалних вода.

In the connection with this water age analysis, based on the radioactive carbon $^{14}C$ method, it should be said that the problem is complex and that increased values are most often obtained so suitable complex corrections should be made. They were not made in this case, so the values obtained for the younger age should be considered more reliable than the data for the older age. On the whole, the obtained results agree with hydrogeological models of most systems as far as the way, direction and water circulation length duration in their reservoirs is concerned, and are very illustrative as far as demonstration of the sustenance of hydrogeological resources is concerned, referring to nowadays and future climatic changes.

## SUSTENANCE OF GEOTHERMAL WATER RESERVOIRS IN SERBIA

The quality of clear drinking groundwaters in their aquifers has been damaged continually by human unconcern and in this way their reserves are reduced directly, while at

the same time the needs for them increase because of the population growth as well as need for food and medical treatment. This very delicate present situation obliges to both rational development and managing of hydrogeological resources with prime obligation to save them, preventing changing their quality for the worse, and reducing, now available reserves, for future generations.

In connection with all this the sustenance of present reserves is the most important thing, first of all with regard to quality and then with regard to preservation of existing reserves and their increase. According to the concept of sustainable development from the point of view of economics, only the things that make profit are sustainable, so this factor must be taken into account. On the other side sustenance of development is reduced to the development based on using local resources. This concept must be valid for hydrogeological resources too, in other words to groundwaters of any kinds.

In consideration of problems that appear in connection with he sustenance of hydrogeological resources the age of ground waters is one of the main parametres pointing out advantage of hydrogeological resources in that respect. Presented results point out that geothermal waters flowing out from investigated occurences, most of which can serve as drinking water, come from atmospheric waters infiltrated in the Earth's crust, namely to nowadays reservoirs as long time ago as their $^{14}C$ age is.

As the age values of most occurences are older than 2000 years, it means that they are practically sterile, because in the period of their infiltration there were no harmful impacts of human activity to atmospheric and ground waters, in other words those waters flow out to the surface nowadays. On the other side, it means, further that by human activity, nowadays more or less polluted atmospheric waters, infiltrating in the Earth's crust in the same way, after travelling through their accumulations will appear on the surface only in as many years' time as the measured $^{14}C$ age is.

This law means that nowadays favourable quality of ground waters, under the condition that no harm is done to accumulations on the way from recharging zone to discharging zone, minimally for several dozen of future generations, namely, for several hundred years. It is valid for artesian aquifers of groundwaters, covered by water impervious rocks. Those are aquifers off all geothermal waters and aquifers of "cold" drinking waters in artesian basins regardless of their geological composition.

## CONCLUSION

The investigation of the age of the hydrogeological resources, namely, main geothermal water occurences from Serbia region by means of $^{14}C$ isotope has given very useful results on the basis of which climatic changes in the previous 40,000 years and their impact on hydrogeological, namely hydrogeothermal systems can be related.

On the basis of above laws it can be concluded that unfavourable climatic changes and the accompanying changes of quality and quantity of atmospheric waters cannot influence geothermal waters in hydrogeothermal systems as far as their quality is concerned, certainly for the period future generations will live in. Climatic changes in our moderate climatic area, can be unfavourable only if rainfall decrease takes place. In that

case decrease of natural phenomena abundance can take place because it is regulated from infiltration–recharging areas. Such unfavourable climatic changes and changing the quality of the atmospheric waters for the worse will influence open aquifers mostly as freatic and carst ones both in the quality of their waters and their reserves.

The practical significance of the obtained results is even more important, because on their basis it can be affirmed that hydrogeological systems with hobbled aquifers in Serbia region are very sustainable as far as the quality and the quantity of their water resources are concerned.

## REFERENCES – ЛИТЕРАТУРА

Craig H., 1961: Standard for reporting concentrations of deuterium and oxygen−18 in natural water.– Science, 133, 1833–1834.

Lamb H., 1977: Climate: present, past and future – Vol. 2: Climate history and the future.– Methuen and Co. Ltd, London, 833 p.

Milanković M., 1941: Kanon der Erdbestrahlung und seine Anwendung auf das Eiszeitenproblem.– Academie Royale Serbe, Section des Sciences Mathemattiques et Naturelles, Tome 3, Belgrade, 633 p.

Milivojević M., 1989: Assessment of geothermal resources of Serbia.– Doctor thesis, Faculty of Mining and Geology, University in Belgrade, 456 p., Belgrade (in Serbian Cyrrilic).

Ronjon F., Viliams M.A.J., 1977. Late Quaternary climatic changes in Australia and North Africa: a preliminary interpretation.– Palaeogeogr., Palaeoclimatol., Palaeoecol., 21, 285–237.

Vaseur G., Lucazeau F., 1983: Bounds on paleotemperatures and paleoclimatic correction. In: R. Haenel & M. Gupta (Eds.): Result of the First Workschop on Standardization in Geothermics. Zentralblatt fur Geolog. u. Palaontologie, Teil 1, Heft 1/2, Stuttgart, 17−24.

Washburn A., 1980: Permafrost features as evidence of climatic change.– Earth Science Rev., 15, 327–402.

Woillard G., 1979: The last interglacial–glacial cycle at Grande Pile in Northeastern France.– Bull. Soc. Belge Geol., 88, 51–69.

## РЕЗИМЕ

## СТАРОСТ ГЕОТЕРМАЛНИХ ВОДА СРБИЈЕ КАО ПОКАЗАТЕЉ КЛИМАТСКИХ ПРОМЕНА

У раду се приказују резултати изучавања старости већине главних појава геотермалних вода са територије Србије изотопским методама која су по први пут вршена у склопу оцене енергетске потенцијалности геотермалних ресурса Србије (Milivojević, 1989), као индикатора климатских промена у претходних неколико десетина хиљада година и њен значај за оцену одрживости хидрогеолошких или подземних водних ресурса уопште.

Старост подземних вода представља временску дужину њиховог боравка у земљиној кори од момента инфилтрације атмосферске воде од које је настала подземна вода, до момента њеног истицања назад у атмосферу.

За одређивање старости хидрогеолошких ресурса, односно подземних вода користе се различити радиоактивни изотопи елемената који се налазе у њима. То су водоник, тј. тритијум T($^3$H), угљеник $^{14}$C, силицијум $^{32}$Si, хлор $^{36}$Cl, аргон $^{39}$Ar, криптон $^{81}$Kr, криптон $^{85}$Kr или однос U/He. Од ових изотопа најпогоднији за одређивање старости су тритијум и угљеник $^{14}$C, док са осталима има потешкоћа. Тритијум је идеални обележивач вода уопште, јер улази у састав молекула воде. Најпогоднији изотоп за одређивање старости подземних вода је радиоактивни изотоп угљеника $^{14}$C, зато што је једини услов да оне садрже растворене бикарбонате.

Методом одређивања старости подземних вода помоћу изотопа $^{14}$C био је обухваћен и један број најпознатијих појава минералних и геотермалних вода, као и један мањи број плитких хладних вода са подручја Србије. Та испитивања су била изведена у периоду 1986–1988. година на 57 узорака (Milivojević, 1989).

На основу добијених резултата испитивања старости данашњих појава хидрогеотермалних ресурса са подручја Србије, може се закључити да је са $^{14}$C могуће старост воде везати за геолошку старост, тј. за млађе одељке квартара. Пошто се помоћу изотопа $^{14}$C може одређивати старост до 40.000 година, то се може доводити у корелацију изотопски састав воде и промене климе у холоцену.

У хидрогеотермалним системима код којих колектори залежу дубоко и имају велико хоризонтално пружање, треба сматрати да климатске промене утичу на процесе прихрањивања и пражњења система. Општа је констатација да су глацијални периоди на већим географским ширинама и висинама били у корелативној вези са периодима мале евапорације и високих падавина на средњим географским ширинама.

Различитим методама је одавно доказано да се у току квартара клима често и знатно мењала тако да су се смењивала ледена и топла доба, тј. глацијациони и интерглацијациони периоди (Milanković, 1941). После задње глацијације промене климе су знатно мање, оне се јављају у задњих неколико хиљада година и продужавају до данас.

Може се закључити да је већина резервоара хидрогеотермалних система била интензивно пражњена за време хладних периода између 20.000 и 10.000 година пре нове ере, јер су падавине биле мале а подручја прихрањивања залеђена и због тога водонепропусна. Прихрањивани су кад су преовлађивали супротни климатски услови, односно у периоду између 10.000 и 5.000 година пре нове ере.

Садржај стабилних изотопа у водама метеорског порекла директно зависи од климатских фактора. Подземне воде у вишегодишњим интервалима одражавају углавном просечне локалне климатске услове који условљавају скоро константан садржај стабилних изотопа. Међутим, свака значајнија климатска промена у неком временском периоду, који је дуг у поређењу са изравнањем изотопског састава локалне издани, биће обележена променом садржаја стабилних изотопа. Општа констатација је да мали садржаји $\delta^{18}$O и $\delta^{2}$H у односу на садржај истих изотопа у данашњим падавинама означавају хладне и влажне палеоклиматске периоде.

У вези са горе изнетим зависностима и констатацијама израђени су дијаграми на којима су приказане вредности $\delta^{2}$H и $\delta^{18}$O у испитиваним водама са поменутом палеоклиматском поделом. Са слика 2 и 3 се види да се прихрањивање скоро свих нискотемпературних отворених карстних конвективних система и система са резер-

воарима у гранитоидним масивима извршило при крају последњег влажног периода и после њега. Најмањи број испитиваних вода потиче из најстаријег влажног периода чија је реконструкција преко садржаја $^{14}C$ мање сигурна у интервалу од 25.000–40.000 година пре нове ере.

У целини, добијени резултати се добро слажу са хидрогеолошким моделима већине система по питању начина, правца и дужине трајања циркулације вода у њиховим резервоарима и веома су илустративни по питању доказивања одрживости хидрогеолошких ресурса у односу на садашње и будуће климатске промене.

Обзиром на проблеме који се испољавају у вези са одрживошћу квалитета површинских водних ресурса, и плитких хидрогеолошких ресурса, старост подземних вода је један од главних параметара који показује предност дубоких хидрогеолошких, а нарочито хидрогеотермалних ресурса у том погледу.

Приказани резултати указују да подземне воде, које сада истичу на испитиваним појавама, потичу од атмосферских вода које су се инфилтрирале у земљину кору пре онолико времена колико износи $^{14}C$–старост. Пошто су вредности старости за већину појава веће од 2.000 година, то значи да су оне практично стерилне, јер у време њихове инфилтрације није било никаквих штетних утицаја људске активности на атмосферске и подземне воде. С друге стране, то значи да људском активношћу, загађене атмосферске воде, које се инфилтрирају у земљину кору, ће се после проласка кроз њихове подземне акумулације појавити на земљиној површи тек за онолико година, колико износи измерена $^{14}C$–старост. Ова законитост значи да ће се садашњи повољан квалитет подземних вода, под условом да се насилно не погорша од стране људи на путу од зоне прихрањивања до зоне истицања, задржати минимално за неколико десетина будућих генерација, односно, минимално неколи-ко стотина година. Она важи за сапете издани. Таква су налазишта свих геотермал-них вода и налазишта–издани питких вода у артеским басенима без обзира на њихов геолошки састав.

На основу горњих законитости може се закључити да неповољне климатске промене и пратеће промене квалитета и количина атмосферских вода не могу утицати на хидрогеолошке ресурсе у обиму хидрогеотермалних система када се ради о њиховом квалитету, сигурно за период у коме ће живети наредне генерације. Промене климе у нашем умереном климатском појасу, када се ради о њиховом утицају на хидрогеолошке ресурсе, могу бити неповољне само ако буду у правцу смањења падавина. У том случају може доћи до смањења издашности природних појава, јер је она регулисана из подручја инфилтрације–прихрањивања. Овакве неповољне промене климе и погоршање квалитета атмосферских вода на подручју Србије ће највише утицати на отворене издани, као што су фреатске и карстне, како у погледу квалитета њихових вода, тако и у погледу резерви.