

INDUSTRIAL TRACER APPLICATION
IN PEOPLE'S REPUBLIC OF CHINA

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ABSTRACT

A number of important applications of radioisotopes and their compounds used as tracers in petroleum industry, metallurgical industry, mechanical industry, chemical industry, electronic industry, hydrology and water conservancy in China are introduced in this paper. And the tracer technique applied to entomology is also mentioned. The industrial tracer applications are successful and beneficial in People's Republic of China from the examples given.

INTRODUCTION

Radioisotopes are essentially ideal and highly sensitive tracers due to the properties of "isotope" and their easily measurable radiations. The production and supply of various radioisotopes and their compounds in large amounts present use with the possibility of wide applications of tracer technique in different fields. In fact, the applications of tracer technique have already been widely spreaded in developed countries in the world. Most industries have recognized the importance and advantages of tracer technique in optimizing plant operation, improving use of materials, improving quality control and increasing industrial competitiveness.

The application of isotope technique in China started in 1950's. In 1957 the Institute of Physics of the Chinese Academy of Sciences began running a Training Course on the Application of Isotopes. In 1958, the first nuclear reactor and the cyclotron were put into operation in the same institute, now called the Institute of Atomic Energy. Since then China has been producing her own radioisotopes to meet the increasing demand in different fields. Thus the applications of radioisotopes in China began developing

at a faster speed. The applications of tracer technique to industry also developed gradually. Under the guidance and support of the State Science and Technology Commission and the Ministry of Nuclear Industry, the tracer technique is now being applied to petroleum industry, metallurgical industry, mechanical industry, chemical industry, electronic industry, hydrology and water conservancy, etc.

TRACER APPLICATION IN PETROLEUM INDUSTRY

The application of tracer technique to petroleum industry in China consists mainly of the measurement of water intake profiles of water injection wells, the determination of the distribution of a corrosion retardant agent in natural gas pipeline, the location of leaks in underground oil pipeline and the "diagnosis" for tertiary recovery.

A. The Measurement of Water Intake Profiles of Water Injection Wells

As early as in 1957, the tracer well logging was started in Yu Men Field, measuring the water intake profiles of injection wells. At that time, radioactive isotope ^{65}Zn imported from the Soviet Union was used. At the beginning of 1960's the Da Qing Field first started using home-made radioisotopes for the measurement. In 1973, charcoal adsorbed ^{131}I was first used as tracer for measuring the profile in Sheng Li Field. In 1983, a new tracer ^{131}Ba labelled microspheres (trade name: $^{131}\text{Ba-GTP}$) was used in Da Qing Field. It was developed by the Institute of Atomic Energy¹ in cooperation with the Da Qing Field.

The $^{131}\text{Ba-GTP}$ is prepared by means of a microsphere technique. It has a hydrophilic and oleophobic surface but inside of it appears as a porous struc-

ture. Its granule specific gravity is 1.00--1.06g/cm³, very close to water's. The grain size can be controlled in preparation according to the oil bearing strata porosity. The rigidity of the ¹³¹Ba-GTP comes to such a level that there is no change in shape and no broken bits observed under the pressure of about 400 kg/cm². Its temperature stability is good between -20--70°C. The specific radioactivity of it is about 5--10mCi/l ¹³¹Ba-GTP. Owing to the fact that the ¹³¹Ba nuclide are firmly combined in the microspheres, there is no evident activity desorption under high speed water flushing before a period of time, such as 6--10days. Besides, the microspheres are soluble in pressurized water flow sometime after injection so that they won't choke the oil bearing strata.

With ¹³¹Ba-GTP as the tracer, the results of the measurement were quite good. The typical results of the measurement with tracer technique have revealed the following points².

a) The measurement of water intake profiles of water injection wells with tracer technique can provide the petroleum production engineers with the water intake information in different strata accurately and directly.

b) The water intake profiles determined with tracer technique can be used as a reliable basis for the evaluation of strata and for the readjustment of water injection programme and checking its effectiveness.

c) They can also be used to find the channels (if any) between strata behind the casing pipe.

d) Likewise, they can be used to solve some engineering problems, such as the locations of the breaking spots in casing pipe, etc.

In recent years, the tracer technique has been applied to many petroleum fields in China. Now, the number of well-time of water injection wells measured per year is in the thousands.

B. The Determination of the Distribution of Corrosion Retardant Agent in Natural Gas Pipeline

In natural gas, there is a small amount of hydrogen sulphide which would corrode the transport pipeline and sometimes may cause serious accident. The

conventional method is adding in a corrosion retardant agent to protect the pipeline from corrosion.

In order to find out the reasonable distance between two inlets of the agent, the amount of the agent added through the inlets every time, and the time interval between two additions, experiments had been done in different conditions with tritium labelled agent as a tracer. The project was completed by the Institute of Atomic Energy in cooperation with the Division of Transportation of Natural Gas, Bureau of Petroleum Industry Management in Sichuan in 1984. Then, in 1985, the technique was applied to a natural gas transport pipeline in the eastern part of the province. Last September it was further applied to another gas transport pipeline in the same province again.

C. The Location of Leaks in Underground Oil Pipelines

Research work in this field was started in 1965 in China⁴. The Shanghai Institute of Nuclear Research firstly developed the method of locating leaks in underground oil pipeline with radioactive tracers. Detection instruments and device, such as leak detector (both ball type and cylinder type for 6 and 8 inch diameter pipeline) and readout device, have been designed, manufactured and assembled successfully. The tracers used by them were ¹²⁴Sb labelled triphenyl antimony, (C₆H₅)₃¹²⁴Sb, and ¹³¹I labelled iodo-benzene, etc. The largest location error was 2.5 m for two reference points 1,000 m apart.

Because of the great successes in their field tests, the Institute is now requested to locate leak points in underground oil pipelines for several provinces, besides 4 other oil stations in Shangdong province.

D. The "Diagnosis" for Tertiary Recovery

The tertiary recovery of crude oil is a step of the petroleum exploitation after the steps of automatic crude oil gush and water flooding. The crude oil which could be recovered with enhanced recovery technology in tertiary recovery step is about 4--11% of the total reserve. But before the technology is taken, it is essentially necessary firstly to detect the crude oil reserve remained and its distribution. The tracer technique here is also preferable.

Last year, the Institute of Petroleum Exploitation (IPE) signed a contract with the Institute of Atomic Energy (IAE) on the diagnosis for tertiary recovery. According to the contract, the IAE should provide the IPE with several ^3H labelled compounds such as methane, ethane, propane, tritium gas, tritiated water, etc. The project has just begun.

TRACER APPLICATION IN METALLURGICAL INDUSTRY

The application of tracer technique to metallurgical industry in China started in 1950's, too. Now the main organizations working on this field are the Central Iron and Steel Research Institute, Beijing, the Beijing University of Iron and Steel Technology and the Iron and Steel Research Institute of Anshan Iron and Steel Co.

A. The Tracer Work Carried out by the Central Iron and Steel Research Institute, Beijing

In recent years, the Institute has mainly studied the hot corrosion behavior of some alloys with tracers. One of their projects is the study of the hot corrosion behavior of some Ni-based and Fe-based alloys by means of depositing sodium sulphate containing ^{35}S on the surface of the alloys in the laboratory atmosphere. The autoradiography shows that during the process of hot corrosion the sulphur contained in sodium sulphate was very rapidly reduced to sulphide ions which then diffused along the grain boundaries of the alloy, forming sulphide precipitates there. It was also observed that some sulphides were oxidized to free sulphur which took the precedence of diffusion along grain boundaries into the depth of the alloy. And furthermore, the observation shows that part of the released sulphur diffused into grain lattices. Besides, they have measured the distribution curves of the radioactivity along the depth of alloys and have observed the phenomenon of "uphill" diffusion of sulphur in the oxide film of the alloy. The diffusion coefficients of sulphur in alloys during hot corrosion have been calculated.

Another project is the study of hot corrosion behavior of some Ni-based superalloys containing Nb. It has been found that Nb is enriched in the surface oxide film of Ni-16Cr-2Nb alloy. Nb decreases the O^{2-} activity of Na_2SO_4 melts by the formation of NaNbO_3 , and the

reaction between the Cr_2O_3 film and the melts is then retarded. But for multi-component alloy like In 738 and In 537, Nb might promote acidic fluxing of the oxide film. Nb also promotes continual segregation of sulphur at grain boundaries of Ni-16Cr-2Nb alloy and speeds up the process of internal sulphidation.

Besides, in order to make full use of iron ore and to separate noble metals, the Institute has performed many research projects with radioisotopes as tracers.

B. The Tracer Work Carried Out by The Beijing University of Iron and Steel Technology

The University has performed many research projects with tracer technology and got good results. Some of the projects are as follows.

- a) Study of determining the rare-earth contents in the metal phase of steel
- b) Study of the ascending law of rare-earth inclusions in steel metals
- c) Distribution of the rare-earth inclusions along the depth of steel metals⁵
- d) An investigation of behaviour of cerium in molten iron and its reaction on refractories by means of tracer
- e) Equilibria among rare-earth elements, oxygen and sulfur in molten iron⁶
- f) Determination of diffusion coefficient of cerium in molten slags
- g) Determination of alloyed amount and distribution of Ce in commercial pure aluminum

C. The Tracer Work Carried Out by The Iron and Steel Research Institute of Anshan Iron and Steel Co.

The application of tracer technique in the Institute was started in 1959. Closely integrating with production, the Institute has performed several projects based on the application of tracer technology. Some projects are as follows.

- a) Study on the effect of the ladle lining on the quality of steel using ^{45}Ca as tracer

They add tracer ^{45}Ca into ladle lining material and determine the radioacti-

vity of the slag and nonmetallic inclusion in the steel after the ladle is used. The results obtained show that the alumina-magnesia rammed whole lining is better than the lining made from clay bricks because for the former the erosion is less and the ladle life time is lengthened and the inclusion in the steel is less and the quality of the steel better. According to the study, the alumina-magnesia rammed whole lining ladle has been adopted in converter steel production in Anshan Iron and steel Co. and the annual economic benefit is about 1,350,000 Yuan by saving fire-proof materials only.

b) Study on the movement of gas flow in blast furnace using ^{85}Kr as tracer

From the study, the following results have been obtained.

- the melting time and distribution of the gas in the furnace,
- the stability of the gas flow in the loaded column,
- the dynamics of the gas flow along the height of loaded column, and
- the void content of the loaded column.

This study is very valuable for the improvement of the blast furnace operation and increasing the productivity.

c) Study on the effect of calcium on the nozzle clogging in pouring aluminum killed steel

From the study, they found that the calcium content in ferro-silicon alloys was one of the main causes of nozzle clogging. And the nozzle clog has disappeared basically when the total amount of calcium was strictly kept less than 0.5%. One of the three steelmaking works has adopted this percentage and makes an economic benefit of about 520,000 Yuan per year.

TRACER APPLICATION IN MECHANICAL INDUSTRY

Tracer technique is also applied to mechanical industry in China. Kryptonization, mechanic wearing and leak detection are the main projects and the Shanghai Research Institute of Materials and the Beijing Oriental Scientific Instrument Factory are the main organizations.

A. The Application of Kryptonization Technique

In a kryptonization chamber ^{85}Kr is diffused into a kind of materials such as metal or a part of a machine by means of diffusion or ion bombardment so that the metal or the part becomes labelled.

After kryptonization, the article hasn't changed its original chemical property but has got a special character. It will release ^{85}Kr increasingly with temperature but after that it won't release any ^{85}Kr at temperatures below the highest temperature ever reached before. However, if the temperature goes to higher than this level it will release ^{85}Kr again. Accordingly the highest working temperature and temperature distribution of a part, especially a dynamic part of a mechanism can be easily and correctly determined. This can't be realized by means of any other method.

The Shanghai Research Institute of Materials has applied this technique to determine the highest working temperature and temperature distribution of the exhaust valve of the engines CA10B of a truck for Changchun Automobile Factory, and the highest working temperature at the top of a needle valve stem of the oil nozzle ZS4SJ1 of an engine for a factory in Shanghai. Some parts of mini-bearing, turbo-generator, internal combustion engine, textile machine, etc have been studied, too.

Combined with autoradiography the kryptonization technique can be used to examine a surface and to study other problems in material science and technology.

B. The Study of Mechanic Wearing

The Shanghai Research Institute of Materials has been studying mechanic wearing of piston rings, needle valves of oil nozzle etc.

The procedure of the wear test is basically as follows.

- Activating the object to a suitable specific activity,
- Cooling the activated object to let the active impurities decay to a negligible level, and
- Conducting wear test, to measure every 1-2 hours the ^{59}Fe activity of the worn-off powder and plot the wearing curve,

With the results of the study, it

becomes possible to evaluate the wearing and suggest how to improve the objects' quality.

C. The Leak Detection

The Beijing Oriental Scientific Instrument Factory has designed and manufactured an equipment for leak detecting with ^{85}Kr gas. It can be used to detect the leakage of different parts, components, and large or complicated systems. It can detect the leakage of a system as a whole or any part of it. The sensitivity of the detection is 10^{-12}mol.atm/s with the precision of 20%. The equipment has been carrying out different leak detections since it was built.

TRACER APPLICATION IN CHEMICAL INDUSTRY

At present, the main application of tracer technique to Chinese chemical industry is the determination of the mercury inventory of electrolytic cells in soda plants with ^{197}Hg isotope dilution⁷.

For a plant the loss of mercury in the electrolytic process has to be regularly examined, since mercury is expensive and pollutes the environment. Gravimetric method has been the conventional method. But by this conventional method, the production must be stopped and the mercury has to be drained out for weighing balance by balance and cell after cell. It is a rather laborious and time-consuming job with loss of productivity. Furthermore, the results are not very accurate because a significant amount of mercury is trapped in the cell system, and the mercury vapor will diffuse out into the environment because so much mercury is exposed to the air.

The ^{197}Hg isotope dilution method is quite different. It is sensitive, accurate, without stopping of production, no extra mercury vapour contamination, easy and quick.

The IAE has determined the mercury inventory of the electrolytic cells for several soda plants with the method so far.

TRACER APPLICATION IN ELECTRONIC INDUSTRY

The Fu Dan University in cooperation with a semiconductor device factory has developed a method of detecting the leakage of semiconductor devices (including transistors and integrated circuits) with ^{85}Kr gas.

The sensitivity of the detection reaches 10^{-11}mol.atm/s with the precision of about 30%. The method is not only sensitive but also easy and fast, hundred times faster than the mass spectrometer method. Since the method was developed, it has been applied to the leak detection in regular production of semiconductor devices. Besides, the method is also useful for the leak detection of relays, electric condensers, electronic tubes etc.

TRACER APPLICATION IN HYDROLOGY AND WATER CONSERVANCY

The tracer technique applied to hydrology and water conservancy and hydraulic engineering in China is mainly concentrated on the investigations of the groundwater movement, the sediment transport in rivers and estuaries, the river discharge measurement and the investigation of seepage in earthfill dams of water reservoirs. Most of the tracers used are artificial though stable and environmental isotopes have been in increasing use in isotope hydrology. There are many institutions more or less involved in related research in these fields in China but the main ones are the Nanjing Hydraulic Research Institute and the Institute of Water Conservancy of the Yellow River Conservancy Commission, etc.

A. The Investigation of Groundwater Movement

Single-well technique with artificial radioisotope as tracer has been used to determine the groundwater velocity and direction. The principle of the determination is based on dilution. Most of the devices used are self-made. Beside the Nanjing Hydraulic Research Institute, Jiangsu Agronomy Research Institute and Beijing Environmental Protection Research Institute etc are also engaged in the investigation.

B. The Investigation of the Sediment Transport in Rivers and Estuaries

Several investigations have been carried out in the Zhenjiang Harbour, the Hangzhou Bay, the estuary of the Yangtze River and the estuary of the Yellow River by the Nanjing Hydraulic Research Institute and the Institute of Water Conservancy of the Yellow River Conservancy Commission. The tracers used were ^{46}Sc , ^{113}mIn etc. These investigations have provided information for locating the dock, reconstruction of the harbour, dredging the sediment out and pre-

venting sedimentation.

Many other research works on sedimentology have been done by the Xiamen (Amoy) Institute of Oceanography.

C. The Measurement of River Discharge

Tracer dilution method has been used for the river discharge measurement. Experiments have been done in the Yellow River by the Institute of Water Conservancy of the Yellow River Conservancy Commission. The tracer ^{169}Yb was used by means of instantaneous injection. The mixing length was about 4,000 m.

D. The Investigation of Seepage in Earthfill Dams⁸

Since 1974, several earthfill dams of 9 unsafe water reservoirs in China have been investigated by means of single-borehole and multi-borehole techniques with Na^{131}I solution as tracer. The total capacity of the 9 reservoirs is about 3.9 billion m^3 and the total irrigation area is about 0.29 million ha. By the results of the investigations, suitable proposals of how to improve them and measures to be taken have been adopted by concerned authorities. Those reservoirs are normally working again. Large amounts of investments have been saved. Otherwise, expensive measures would have to be taken, including even building new dams instead of improving the old ones.

There are more than 86 thousand reservoirs in China and ~90% of them are earthfill dams. Seepages in the dams are happening now and then. The tracer technique, having been proved to be an effective and time-saving method, will further play its important role in this field.

TRACER APPLICATION IN ENTOMOLOGY

Termite is a kind of the pests worldwide. Termites could damage almost all kinds of materials in various areas of economy, such as rubber, plastics, cloth, antiques, communication cables, railway-sleepers, buildings, crops and even forest. The termites with black wings are much more harmful. They could even cause dam failure and result in disaster. But the activities of termites are usually invisible.

Using tracer ^{131}I or ^{198}Au , the Guangdong Institute of Entomology has studied the distribution, damaged parts,

foraging behavior of termites and the effect of the application of insecticides. The investigations have shown that the tracer technique is very sensitive and effective for the detection and control of termites.

CONCLUSION

Radiotracers are very useful means for investigations in industries under a variety of conditions. The applications of them can help obtain information of industrial processes, improve production procedure and management, optimize operation, improve product quality, increase productivity and result in considerable economic and social benefits. The tracer applications in China, as mentioned above, have been proved to be successful. It is expected that the tracer technique will be further expanded and developed at a faster speed in China.

ACKNOWLEDGEMENT

The author would like to thank all the personnel for their valuable assistance, support and cooperation. The author would like also to express his gratitude to Professor Xiao Lun, Chairman, Science and Technology Committee, Radioisotope Department, IAEA, Department Member of Chinese Academy of Sciences, President, Isotope Society of China, CNS, for his important advice and encouragement.

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