Study on Reaction Mechanism of Coal Hydrogenation by Means of Radioisotope Tracer Technique*

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This paper is concerned with the coal liquefaction mechanism studied by the use of ^3H and ^{14}C tracer techniques. Taiheiyo coal was liquefied using ^3H and ^{14}C labeled solvents or ^3H labeled hydrogen gas. The effects of Ni-Mo- Al_2O_3 catalyst, reaction times and solvents were examined for the reactions at 400°C and under initial H_2 pressure of 5.9MPa. The concentrations of isotopes in the products were determined by a liquid scintillation counter. The hydrogen and carbon material balances were calculated and the amounts of the hydrogen addition and exchange among gas phase, coal products and solvents were estimated. In the process of the primary liquefaction in hydrogen donor solvent, coal was thermally decomposed and hydrogenated by hydrogen atoms mainly released from solvents. However, the primary coal liquids were hydrocracked by hydrogen molecules on the catalyst. When naphthalene was used as the liquefaction solvent in the presence of the catalyst, the hydrogen transfer process through hydrogenation-dehydrogenation of the solvent became important. It is concluded that this tracer technique is useful for evaluating the hydrogen transfer mechanism in coal liquefaction.

1. Introduction

In order to develop practical processes of direct liquefaction of coal, it is important to estimate the rates of hydrogen transfer during the liquefaction. The demonstration scale process is now developing in Japan. As the reactions in this process consist of both the hydrocracking by gaseous hydrogen and the hydrogen transfer from donor solvents, the understanding of these reactions is regarded as significant for the process design.

Generally, coal liquefactions consist of processes, in which coal is thermally hydrocracked and the produced radicals are hydrogenated by hydrogen atoms supplied from the surroundings. **Figure 1** shows the hydrogen transfer model in which coal is liquefied in a representative hydrogen donor solvent, tetralin, under pressurized hydrogen. In this scheme, hydrogen atoms are supplied to coal directly by tetralin (donation) and/or gaseous hydrogen by the aid of the catalyst (spillover), or hydrogen atoms in coal are also used (shuttling). Liquefied products are hydrocracked by gaseous hydrogen to give lighter products on the catalyst. At the same time, naphthalene may be hydro-

genated to tetralin on the catalyst.

Many of the traditional approaches by studying the product distribution under the various experimental conditions have been made^{1)~6)} and a number of attempts were made to elucidate the mechanisms of hydrogen transfer by the use of deuterium tracer, n.m.r. and m.s. methods.^{7),8)} However, a few investigations using radioisotope tracer method have been made. Poutsma, et al.⁹⁾ performed the liquefaction of Illinois coal in a

Fig. 1 Hydrogen Transfer Model in Coal Liquefaction

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bench scale flow system and investigated the behavior of tetralin during the reaction by the use of ^{14}C tracer technique. They found that the grafting of tetralin to molecules derived from coal occurred to some extent. The ^3H and ^{14}C tracer methods, as developed in our laboratory, allow a study of tritium incorporation by addition and exchange into the coal products from the gas phase as well as from the solvent.^{10)~12)} There are some varieties of interpretations for the effects of solvent and catalyst on coal liquefaction. One of them is that the catalysts are effective to regenerate the donor solvents which are dehydrogenated during the liquefaction.^{1)~5)} On this point of view, Moritomi et al.¹⁾ studied the hydrogen transfer at the initial stage of liquefaction. Another states that solvents are effective only to disperse coal and catalyst particles and to dissolve gaseous hydrogen and then catalysts act to hydrogenize coal and coal products by the use of gas phase or dissolved hydrogen.⁶⁾

In this report, the results from the former reports^{10)~12)} are summarized together with some new understandings given by the experiments under ^3H -labeled gaseous hydrogen and in some variety of solvents.

2. Experimental

2.1 Materials

Taiheiyo coal (C 77.2, H 6.7, N 1.1, S 0.2, O 14.9 wt% daf, ash 16.1 wt% dry basis) was ground, sieved through 150 mesh and dried at 100°C for about 5 h under 1 mmHg. Tetralin, toluene and

naphthalene obtained from commercial source (extra pure grade) are used as the liquefaction solvents without further purification. In some experiments, small amounts of ^3H labeled tetralin and ^{14}C labeled naphthalene were added to unlabeled tetralin and the initial concentrations of ^3H and ^{14}C were controlled to be 60,000 dpm/g and 30,000 dpm/g, respectively. The amount of naphthalene which was added to 75 g of tetralin solvent was about 0.2 g and its role was to be the tracer of naphthalene that was converted from tetralin during the reaction. Tritium labeled hydrogen gas, 500,000–800,000 dpm/g H_2 , was applied to gas phase in some liquefaction reactions. Benzene, hexane, tetrahydrofuran and pyridine which were used as extractants for the fractionation of coal liquefied products were extra pure grade from commercial origin. Commercial Ni–Mo– Al_2O_3 catalyst having MoO_3 content of 15.3 wt%, NiO content of 2.9 wt% and the specific surface area of $197\text{ m}^2/\text{g}$ was calcined at 400°C for about 5 h before use.

2.2 Liquefaction, Separation and Measurement Procedures

The coal liquefaction was performed in a 350 ml autoclave containing 75 g of solvent, 25 g of coal and 0 or 5 g of Ni–Mo– Al_2O_3 catalyst and filled with hydrogen at an initial pressure of 0 or 5.9 MPa. It was heated at a heating rate of $10^\circ\text{C}/\text{min}$ and held at 400°C during the reaction.

The reaction mixtures in the autoclave were separated by filtration, distillation and extraction, as shown in **Fig. 2**. In this diagram, naphtha,

Catalyst, Ni–Mo– Al_2O_3 ; Initial H_2 , 5.9 MPa;
Reaction temperature and time, 400°C and 30 min.

Fig. 2 Material, ^3H and ^{14}C Balances on Liquefaction in ^3H Labeled Tetralin

light oil and SRC were the distilled fractions under 200, 204–350 and over 350°C, respectively. As for the solvent extractions, HS, BS and PS represent hexane, benzene and pyridine soluble products, respectively; HIS, BIS and PIS represent the insoluble ones. SRC was separated into HS (oil), BS-HIS (asphaltenes) and PS-BIS (pre-asphaltenes). The separated gas, coal products and solvents were weighed and analyzed with g. c.. Naphthalene, decalin, methylindan and butylbenzene produced during coal liquefaction are thought to be converted from tetralin solvent, and the recovered yields of the solvent containing them ranged from 97 to 98 wt%.

The specific activities of ^3H and ^{14}C in the reaction products were measured with a liquid scintillation counter. Colorless or light colored products were directly dissolved into the scintillator, while the colored liquid, solid and gas were oxidized to H_2O and CO_2 to avoid color quenching.

3. Results

3.1 Liquefaction in ^3H Labeled Tetralin

Figure 2 shows the separation process of products; material balances of products, ^3H and ^{14}C were obtained in the flow of separation process as shown in Fig. 2. Specific radio activities of ^3H and ^{14}C of solvents and coal products in Fig. 2 suggest that ^3H was transferred from tetralin to the reaction products but the transfer of ^{14}C , except to tetralin, was little during the liquefaction. The ^{14}C transfer to the liquefaction products was only 1.6% of the total ^{14}C , even in the another experiment at 440°C, so that it is considered that the

incorporation of the solvent molecule to coal products scarcely occurs. The yield of hydrogenation of naphthalene can be evaluated using the amount of ^{14}C transferred from naphthalene to tetralin. The amount of ^{14}C which was contained in tetralin after the liquefaction with the catalyst, at 400°C and for 30 min was about 1.2% of total ^{14}C and the remaining ^{14}C was left in naphthalene. The rehydrogenation of naphthalene to tetralin, therefore, was little during the primary liquefaction step within 30 min and the hydrogenation-dehydrogenation reactions between tetralin and naphthalene was little. When the liquefaction was conducted at 440°C and for 120 min, the amount of ^{14}C transfer was much larger (18%)¹¹⁾, which suggested the faster rehydrogenation of naphthalene to tetralin in 440°C than 400°C.

The hydrogen addition and exchange reactions between tetralin and gaseous hydrogen without coal were also examined using ^3H labeled tetralin solvent and unlabeled gaseous hydrogen under the same liquefaction condition. In the absence of coal, 12% of tetralin was hydrogenated to decalin by gaseous hydrogen and 3% of tetralin was converted into naphthalene at 400°C and 30 min. The observed ^3H distribution, 84.4% in solvent and 15.6% in gas, agreed with the calculated value, 16.0%, assuming the complete scrambling of hydrogen atoms between solvents and gaseous hydrogen. When the same experiment was conducted without catalyst, neither hydrogen addition to solvent from gas phase nor any ^3H exchange was observed. Under the experimental conditions at 400°C and 30 min, therefore, the disproportiona-

Fig. 3-a and -b Effect of Reaction Time on the Product Distribution for the Liquefaction in ^3H Labeled Tetralin

○, tetralin; ■, SRC; □, gas; ●, naphtha; △, light oil;
The reaction conditions are the same as Fig. 3.
Fig. 4-a and -b Effect of Reaction Time on the Tritium Distribution
for the Liquefaction in ^3H Labeled Tetralin

tion of tetralin to naphthalene and decalin is less than 3% of tetralin in the presence of the catalyst and 0% in the absence of catalyst.

Figure 3 shows the effects of reaction time and the catalyst on the product distributions for the experiments using ^3H labeled tetralin and unlabeled gaseous hydrogen. The product distributions indicate that the catalyst enhances the hydrocracking of preasphaltenes to oil and asphaltenes. **Figure 4** shows the amounts of ^3H transferred to the same products as in **Fig. 3**. The amount of tritium in gaseous hydrogen is significantly smaller than the equilibrium value, 13%, of tritium exchange among gaseous hydrogen, coal and solvent. Besides, even in the presence of the catalyst, this value does not increase in the course of the reaction, thus coal or coal liquids may inhibit the hydrogen exchange reaction between gaseous hydrogen and tetralin on the catalyst. **Figure 5** shows the concentrations of naphthalene produced during coal liquefactions in the presence and absence of the catalyst. In the presence of the catalyst, the concentrations of naphthalene formed in only tetralin or in the presence of coal products (HS and BS-HIS) are also plotted in **Fig. 5**. In the presence of coal without the catalyst, the concentration of naphthalene increased dramatically. When the catalyst was introduced, however, it was always lower than that without catalyst. On the other hand, when the experiment was conducted without both gaseous hydrogen and catalyst, the amount of residue was the same as that in the presence of gaseous hydrogen without catalyst.¹⁰⁾ The results suggest that the hydrogen atoms used in liquefaction are largely supplied by tetralin solvent in the primary liquefac-

□, in the presence of coal, catalyzed; ■, in the presence of coal, uncatalyzed; ○, in the presence of oil (HS); ●, in the presence of asphaltene (BS-HIS); △, in the presence of solvent (tetralin); Catalyst, Ni-Mo- Al_2O_3 ; Initial H_2 , 5.9 MPa; Reaction temperature, 400°C.
Fig. 5 Effect of Reaction Time on Production of Naphthalene in Tetralin Solvent

tion of coal under the presence or absence of the catalyst, but the supply of hydrogen atoms from tetralin is depressed in hydrocracking steps of HS and BS-HIS as shown in **Fig. 5**. It means that the hydrogen molecules dissociated on the catalyst are used in the secondary hydrocracking of coal liquids.

In addition, concentrations of decalin remained constant throughout the reaction time, but those of methylindan and butylbenzene increased gradu-

ally, regardless of the presence or absence of the catalyst. It means that decalin is an impurity in tetralin and others are converted from tetralin during the reaction.

3.2 Hydrocracking of Coal Liquids

Figure 6 shows the product distributions of the secondary hydrocracking of the primary coal liquids: HS, BS-HIS, PS-BIS and unseparated SRC, after the reaction for 120 min, at 400°C, in tetralin, under pressurized H₂ and in the presence of the catalyst. HS and BS-HIS mainly produce light oil and HS, respectively. It is shown that in the presence of BS-HIS, the hydrocracking of HS to light oil is somewhat depressed. PS-BIS is hydrocracked to produce BS. From another experiment in which the reaction time was varied, it was shown that the amounts of HS and light oil remained almost constant during the reaction of PS-BIS and, at the same time, PS-BIS decreased and BS-HIS was produced at constant rate. From these results, it is considered that the presence of PS-BIS depresses further hydrocracking of BS-HIS or HS.¹³⁾

In **Fig. 6**, the components of the source SRC is shown. Then, a calculation can be made to elucidate what composition should be given when each component of SRC is hydrocracked independently and put together in the proportion of the source composition. The calculated result is shown by SRC_{calc} and compared with the result of the hydrocracking of the unseparated SRC (source SRC). From the comparison, the following results

N, naphtha; L, light oil; HS, HS; BS, BS-HIS; BIS, PS-BIS; SRC_{calc}, Calculated from the data of HS, BS-HIS and BIS and these contents in source SRC

Fig. 6 Product Distributions in Hydrocracking of Coal Liquids

Initial H₂, 5.9 MPa; Reaction temperature and time, 400°C and 30 min.

Fig. 7 Products and ³H Distributions in Coal Liquefaction in Tetralin Solvent under ³H Labeled H₂

are shown: (1) The presence of PS-BIS in the system largely depressed the hydrocracking of BS-HIS to HS and (2) the hydrocracking of PS-BIS takes precedence over that of BS-HIS. These results are considered to show that the heavier coal products are more adsorbable on the catalyst and have the priority to react there.

3.3 Reactions under ³H Labeled Gaseous Hydrogen

Figure 7 shows the distributions of products and ³H after the liquefaction in the system of ³H labeled gaseous hydrogen and unlabeled tetralin at 400°C for 30 min with or without the catalyst. In the presence of the catalyst, the amounts of ³H incorporation into liquid products are larger than in the absence of catalyst. These increases of the incorporation are due to the hydrocracking of the liquid products using gaseous hydrogen and the hydrogen exchange between gaseous hydrogen and coal products.

The effect of solvents during the liquefaction was also examined by the use of toluene and naphthalene solvents in ³H labeled gaseous hydrogen. The distributions of products and ³H are shown in **Figs. 8** and **9**. Toluene was used as a sample of a solvent which is less active as a hydrogen donor and naphthalene was used as a sample which can change to hydrogen donor, namely tetralin.

From the comparisons of **Figs. 8** and **9** with **Fig. 7**, toluene and naphthalene are inferior solvents for the liquefaction without catalyst, but they give good results with the catalyst. In the case of toluene solvent, the amount of ³H transferred to solvent is the least among the three solvents, but ³H transfer to coal products in the presence of

Initial H_2 , 5.9 MPa; Reaction temperature and time, 400°C and 30 min.

Fig. 8 Products and ^3H Distributions in Coal Liquefaction in Toluene Solvent under ^3H Labeled H_2

Initial H_2 , 5.9 MPa; Reaction temperature and time, 400°C and 30 min.

Fig. 9 Products and ^3H Distributions in Coal Liquefaction in Naphthalene Solvent under ^3H Labeled H_2

catalyst is the largest. In the case of naphthalene solvent, the amount of ^3H transferred to solvent is larger compared with the case of tetralin solvent with the catalyst. It is concluded that, in toluene solvent, hydrogen atoms used for the coal liquefaction are supplied from gas phase directly, but in naphthalene solvent, they are supplied from gas phase partly through the solvent. It is regarded that tetralin produced by the rehydrogenation of naphthalene is dehydrogenated immediately by coal and it converts to ^3H containing naphthalene. The hydrogen transfer cycle of naphthalene→tetralin→naphthalene is very effective in the liquefaction in naphthalene solvent. That is why ^3H content in naphthalene is high, compared with the case of tetralin solvent and also why ^3H contents in coal products are less than the case of toluene solvent. These results are coincident with those of Moritomi et al.¹⁾ and other workers.^{2)~5)}

4. Discussion

4.1 ^3H Concentrations in Coal Products and Solvents

The concentrations of ^3H in coal products and solvents given in Figs. 7, 8 and 9 are shown in Fig. 10. In the case of naphthalene solvent, ^3H concentration in tetralin is the largest in the solvent fractions and it corresponds to the value which is given when naphthalene is hydrogenated by two ^3H labeled hydrogen molecules. On the other hand, ^3H concentrations in unchanged solvents are small. This means that the hydrogen exchange between solvents and hydrogen molecules is minor and the amount of exchange is less than a few percent of the solvent hydrogen atoms even in the presence

Reaction temperature and time, 400°C and 30 min.

Fig. 10 Tritium Concentrations in Liquefied Products and Solvents

of the catalyst.

However, ^3H concentrations in coal products are much larger and, in the case without catalyst, its order : Toluene > Naphthalene > Tetralin, is showing to be the reverse order of the hydrogen donating qualities of these solvents. The ^3H concentrations in coal products are also the same order in the presence of the catalyst. It suggests that, in toluene solvent, the liquefaction proceeds with hydrogen spillovers from hydrogen adsorbed on the catalyst, but, in naphthalene solvent, coal is liquefied by hydrogen donation from tetralin converted from naphthalene.

In addition, in the absence of catalyst, ^3H concentrations in heavier coal products are larger than that in lighter coal products. This agrees with Heredy's results.⁷⁾ The reason is not clear but it seems that the heavier products have much more mobile hydrogen atoms such as OH or NH and these hydrogen atoms are able to exchange with hydrogen molecules even without catalyst.

4.2 Hydrogen Transfer Mechanism

From the data of **Figs. 3, 4, 5, 7 and 9**, we can calculate the amount of hydrogen transferred by addition or exchange reactions among gaseous hydrogen, solvent and coal products. The calculated results are shown schematically in **Fig. 11**, in which the solid and dotted arrows indicate the directions of hydrogen addition and exchange among shown phases, respectively. In these calculations, following assumptions were made on the bases of above experiments.

(1) The hydrogen exchange between gas phase and solvent does not proceed under a condition without catalyst, because it was found that no hydrogen exchange occurred in the absence of both coal and catalyst.

(2) The amount of hydrogen added to solvent from gas phase is equal to the amount used for hydrogenations of naphthalene to tetralin. This value can be calculated from the amount of ^{14}C transferred from naphthalene to tetralin, about which was described in the former section (**Fig.5**).

(3) On the reactions in ^3H labeled solvent, the amount of hydrogen exchange between gaseous hydrogen and coal in the presence of a catalyst is at least larger than that in its absence. On the other hand, under ^3H labeled gaseous hydrogen, the amount of hydrogen exchange between coal and solvent in the presence of a catalyst is at least greater than in its absence.

The ^3H transfer between hydrogen molecules and solvents with a catalyst must be considered to occur by two pathways, one is the direct path between hydrogen molecules and solvents and the other is through coal to solvents or to hydrogen molecules.

The data presented in **Fig. 11** illustrate that the catalyst slightly decreases the hydrogen addition from solvent to coal but that it considerably increases that from gas phase to coal products. The latter increased with reaction time. This increase of hydrogen consumption is considered to be equal to the amount used for the hydrocracking of the coal liquids, because the yields of the liquefaction, which are calculated from the amounts of unconverted coal, are almost the same in both cases with and without the catalyst. As shown before in Section 3.1, when coal and/or heavy coal liquids are present, however, the hydrogenation of solvents by gaseous hydrogen is rather little even in the presence of the catalyst compared with the case of hydrogenation of solvents in the absence of coal. In other words, the hydrogen exchange between gaseous hydrogen and solvents

Fig. 11 Diagram of Hydrogen Transfer in Taiheiyo Coal Liquefaction

is suppressed since solvents cannot easily be adsorbed on the catalyst in the presence of the heavier coal products. The hydrogen exchange between gas phase and coal products, on the contrary, proceeds considerably even in the absence of catalyst. This result means that there are many transferable hydrogens in the coal products which are easy to exchange with gaseous hydrogen but are difficult to exchange with hydrogen atoms in solvent molecules.

5. Concluding Commentaries

The mechanism of hydrogen transfer during the coal liquefaction was determined using ^3H and ^{14}C tracers and the following results were obtained.

(1) In the process of the primary liquefaction, coal is thermally decomposed and hydrogenated by the hydrogen atoms released from hydrogen donor solvent.

(2) In the process of the hydrocracking of primary coal liquids, the coal liquids are hydrocracked on the catalyst by hydrogen atoms mainly supplied from gaseous hydrogen.

(3) The hydrogen exchange between solvent and gaseous hydrogen during coal liquefaction is little even in the presence of the catalyst.

(4) The heavier coal liquids are more adsorbable on the catalyst surface, so that the hydrocracking of these heavier products take the precedence over that of the lighter products.

(5) In naphthalene solvent, only a small amount of coal is liquefied in the absence of catalyst because hydrogen transfer from both solvent and gaseous hydrogen is difficult. But, the liquefaction in naphthalene in the presence of the catalyst proceeds much faster, because of the hydrogen transfer cycle of naphthalene→tetralin→naphtha-

lene due to the hydrogenation of naphthalene in the presence of the catalyst.

(6) The distinction between hydrogen addition and exchange among gas phase, solvent and coal products can be made clear by these series of experimental methods using radioisotope tracers.

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要 旨

ラジオアイソトープトレーサー法による石炭の水素化分解反応の作用機構の解明

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^3H および ^{14}C でラベルした溶媒または ^3H でラベルした気相水素を用いて太平洋炭の液化を行い、この反応に伴う石炭成分、気相、溶媒間の水素原子の移行（付加および交換）を追跡した。反応は主に 400°C 、水素初圧 5.9 MPa で行い、石炭の液化または一次液化油の二次水素化反応における生成物分布および生成物中の ^3H および ^{14}C 量の分布に対する Ni-Mo- Al_2O_3 触媒、反応時間および溶媒の効果を調べた。溶媒としては水素供与性を持つテトラリン、それ自体では水素供与性はないが反応系内で水素供与性溶媒に変換可能なナフタレンおよび水素供与性の小さいトルエンを用いた。

その結果、石炭液化反応では石炭自身が熱分解して溶媒に溶けていく一次液化と触媒上で水素化分解されて軽質留分に変化して行く二次水素化分解に分けて考えられ、これらの反応に対するラジオアイソトープトレーサー法からの知見は以下のよう

にまとめられた。

(1) テトラリン溶媒中に少量の ^{14}C でラベルしたナフタレンを加えて行った液化反応の結果から、溶媒から石炭分解生成物への炭素原子の移行はほとんど起こらないが、触媒が共存する系では石炭液化で生じるナフタレンの一部がテトラリンに再水素化され、この再水素化の割合はテトラリンへ移行した ^{14}C の量から追跡できることが示された (Figs. 2, 5)。

(2) 触媒上での水素化分解は液化生成物中の重質成分（例えばプレアスファルテンやアスファルテン）が優先し、重質成分の共存下では軽質成分（例えばオイルや灯軽油）の水素化分解は抑制される。従って灯軽油等の軽質成分収量を増すためには一次液化油である SRC をプレアスファルテン、アスファル

テン、オイルに分別後、各成分ごとに水素化分解を行うのがよいことが示された (Fig. 6)。

(3) 気相水素と溶媒水素の間の交換反応は触媒が共存する反応条件下では石炭が不在であれば速いが、石炭成分の共存によって強く抑制される。

(4) 気相水素を ^3H でラベルした実験では、触媒共存下で溶媒中に移行した ^3H はナフタレン<テトラリン<トルエンの順に増加し、石炭成分中に移行した ^3H 量はトルエン中が最大であった (Figs. 7, 9, 10)。

(5) 水素供与性のないトルエン溶媒中では触媒が共存することにより一次液化も二次水素化も、ともに気相水素から直接水素供与を受けて進行する。これは石炭内部の反応と考えられる一次液化でも触媒の作用により気相水素がスピルオーバーする機構が存在することを示している (Fig. 9)。

(6) ナフタレン溶媒中では触媒が無いと液化率は低く抑えられるが触媒の共存により気相水素が反応に関与するようになり、このとき気相から溶媒中に移行した ^3H 量が多くなる。これは、ナフタレンを水素化して生じたテトラリンが石炭の液化を促進しているためと考えられる。また、この機構はナフタレン溶媒中の反応では石炭成分中に移行した ^3H 量はトルエン溶媒の場合より低いことから支持される (Fig. 10)。

(7) 最後に、気相-溶媒-石炭成分間の水素移行量を付加反応によるものと交換反応によるものとに分離する計算を行い、気相水素および溶媒水素の移行量に対する溶媒および触媒の効果を明らかにした (Fig. 8)。

Keywords

Carbon-14 tracer method, Coal liquefaction, Hydrogen transferable solvent, Nickel molybdenum, Taiheiyo coal, Tritium tracer method