Water Chemistry Data Acquisition, Processing, Evaluation and Diagnosis Systems for Nuclear Power Reactors

Shunsuke Uchida[1*], Kenkichi Ishigure[2], Hiroshi Takamatsu[3], Hideki Takiguchi[4], Motoyasu Nakagami[5] and Makoto Matsui[6]

[1] Tohoku University, 01 Aobayama, Sendai, 980-8579, Japan
*E-mail address: shunsuke.uchida@qse.tohoku.ac.jp
[2] Saitama Institute of Technology, Fusaiji, Okabe-machi, Osato-gun, Saitama, 369-0293, Japan
[3] Kansai Electric Power Co. 3-3-22, Nakanoshima, Kita-ku, Osaka, 5308270, Japan
[4] The Japan Atomic Power Co.1-1, Kanda Mitoshiro-cho, Chiyoda-ku, Tokyo, 101-0053, Japan
[5] Chubu Electric Power Co. 1, Toshin-cho, Higashi-ku, Nagoya, 461-8680, Japan
[6] Hamaoka NPP, Chubu Electric Power Co. Hamakoka-cho, Ogasawara-gun, Shizuoka, 437-1695, Japan

Data acquisition, processing and evaluation systems have been applied in major Japanese PWRs and BWRs to provide (1) reliable and quick data acquisition with manpower savings in plant chemical laboratories and (2) smooth and reliable information transfer among chemists, plant operators, and supervisors. Precise and reliable evaluations of water chemistry data are required in order to improve plant reliability and safety. For this, quality assurance of the water chemistry data acquisition system is needed. At the same time, theoretical models are being applied to bridge the gaps between measured water chemistry data and the information desired to understand the interaction of materials and cooling water in plants. Major models which have already been applied for plant evaluation are: (1) water radiolysis models for BWRs and PWRs; (2) crevice radiolysis model for SCC in BWRs; and (3) crevice pH model for SG tubing in PWRs.
High temperature water chemistry sensors and automatic plant diagnostic systems have been applied in only restricted areas. Electrochemical corrosion potential (ECP) sensors are gaining popularity as tools to determine the effects of hydrogen injection in BWR systems.

1. Introduction

Water chemistry is not only one of the most important parameters to maintain the plant reliability but also one of the most important indexes to measure plant operational conditions. Water chemistry improvements, *e.g.*, hydrogen water chemistry in BWRs and suitable pH controls in PWRs, have been applied as valuable options for preventive maintenance [1]. Massive amounts of water chemistry data are collected in nuclear power plants to measure the plant operational conditions at every moment. Data acquisition, processing and evaluation systems have been applied in major BWRs and PWRs for reliable and quick data acquisition with manpower savings in plant chemical laboratories and for smooth and reliable information transfer among chemists, plant operators, and supervisors. Though water qualities are different in BWR and PWR systems, the latest data acquisition procedures have much in common in both types[1].

In order to understand plant conditions, *in-situ* measurements for local conditions, *e.g.*, in-core corrosive conditions and crevice water chemistry, are desired. Some mismatchings between the information desired to understand plant conditions and the measured water chemistry data have been reported. From the viewpoint of water chemists, procedures for bridging the gaps as well as providing quality assurance of water chemistry data acquisition are essential subjects.

In this paper, data acquisition and processing systems in BWR plants are introduced as representative for both reactor types, the necessity of quality assurance of water chemistry data is mentioned and then procedures to bridge the gaps between the measured water chemistry data. And then the information needed to understand real interactions between materials and water in the primary cooling systems are described.

2. Major Purposes of Water Chemistry Control

The most important roles of cooling water in light water reactors (LWRs) are as the energy transporting medium and neutron moderating medium. When light water serves as coolant in

nuclear power plants, the resulting high temperature water causes corrosion of structural materials, which leads to adverse effects in the plants, *e.g.*, increasing shutdown radiation, generating defects in materials of major components and fuel claddings, and increasing the volume of radwaste sources [2], [3]. In order to control the adverse effects, it is essential to understand corrosion behaviors of structural materials and then to control them in the LWRs. Corrosion behavior is much affected by the combinations of water qualities and materials. In order to minimize the adverse effects, optimal water chemistry control has been proposed as shown in **Fig. 1** [3].

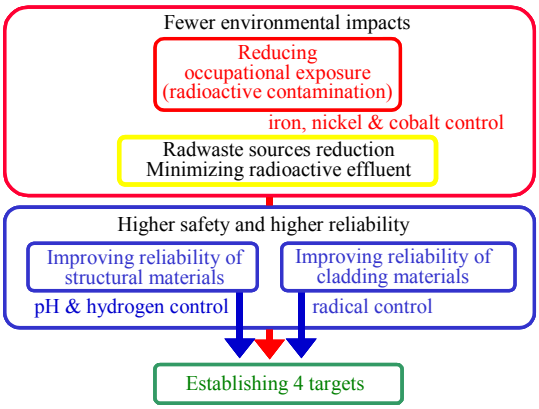

Fig. 1. Optimal water chemistry control (BWR and PWR plants).

3. Water Chemistry Data Acquisition Systems

Nowadays, it is easy to take data from in-line monitors into computer systems, but water chemistry data from the sampled water used to be inputted into the computer systems by plant chemists through keyboard entry. Major improvements have been reported in the latest plants for automatic analysis of chemical and radioactive nuclide data (**Fig. 2**). Chemical species and radioactive nuclides collected on membrane filters are analyzed by X-ray fluorescence analyzers and gamma ray spectrometers, respectively, and then the measured data are transferred from the analyzers to the computer systems directly [1].

Accumulated data are stored in a host computer (data server) allowing easy observation of plant water chemistry. The data numbers are also reduced to be compiled for daily, weekly and monthly documents (reports). Plant chemists, operators and supervisors share the original data and the reduced data through computer networks. On-line ion chromatographs have been applied in plants for fully automatic data acquisition of anion and cation species concentrations, where the data are transferred to the laboratory data server through floppy disks or via direct connection through computer networks [1]. The water chemistry data server is the center of the water chemistry data net work system, which connects with the operation and control computer systems to take plant operational data and to give water chemistry conditions to plant operators.

Trend and transient analyses are critical evaluation procedures. General patterns of the data are compared with those of other plant data. Fuel integrity checking is one of the most important procedures for plant chemists and a major concern for plant operators and supervisors.

In order to evaluate plant conditions by using water chemistry data, two points should be carefully

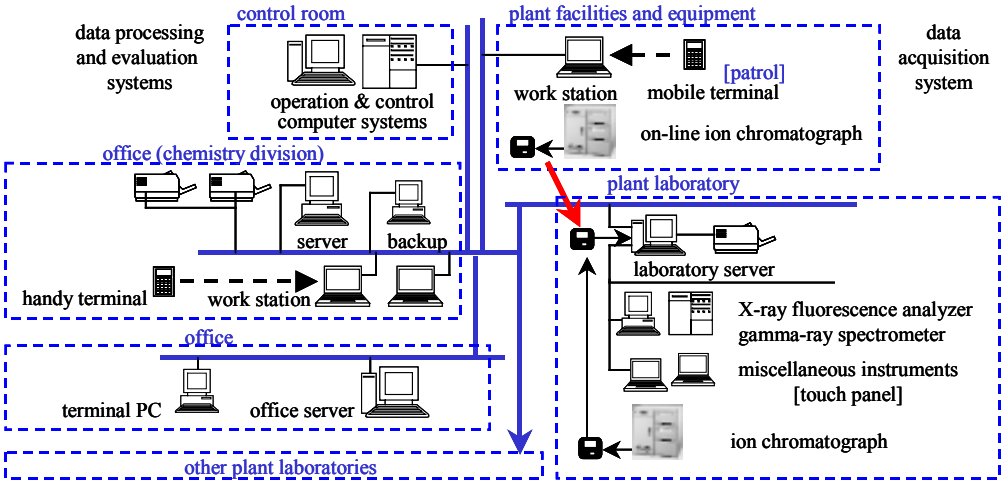

Fig. 2. Water chemistry data acquisition, processing and evaluation systems (BWR plants).

considered. The first point is quality assurance of water chemistry data and the other is bridging the gaps between measured data and desired information.

4. Quality Assurance of Water Chemistry Data

Evaluation should be based on reliable data. For this, quality assurance of water chemistry data is essential. Standardization of data acquisition procedures is required to obtain qualified data, where sampling location and periods, sampling procedures, and analytical instruments to determine chemical and radioactive components, calibration procedures for the instruments and their frequencies, training of plant chemists and documentation guides are clearly defined.

At the same time traceability of water chemistry data is required. For this, standard procedures for document management should be established. Quality assurance of water chemistry data in thermal power plants has been established and the details were published in the Japan Industrial Standards [4].

Enthusiastic promotion of quality assurance of water chemistry data in nuclear power plants based on LWRs and establishment of the standard for acquiring and processing water chemistry data are being carried out as one of the most important activities of the Research Committee on "Water Chemistry Standard" of the Atomic Energy Society of Japan.

5. Beyond Water Chemistry Data

In order to bridge the gaps between measured data and desired information, interactions between water and materials in the plants should be understood clearly. The interactions in BWR plants are listed in **Table 1**.

5.1 Concepts

ECP can be measured in several locations in the primary coolant at elevated temperature and extrapolated to the location of interest to evaluate corrosive conditions of the target structures. Conductivities and pH are measured at room temperature and their effects on the materials should be considered by extrapolating them to values at elevated temperature. One of the most important radiolytic species, H_2O_2, which cannot be measured in the sampled water, should be determined by the theoretical rater radiolysis model along with O_2 and H_2 at the location of interest.

Major gaps between the desired information to understand the phenomena and measured data are shown in **Table 2** with measures to bridge these gaps.

Table 1. Interactions of water and materials (BWR).

Water chemistry factors [operational data]		1) Dose rate reduction	2) Fuel integrity	3) Structure integrity
Macroscopic factors				
pH * room temperature pH	[6 - 8]*	♠ high pH decreases ^{60}Co release from fuel deposits	♥ high pH promotes zircaloy corrosion	♣♦ small effect around neutral pH
Conductivity	[0.1 - 0.3mS/cm]	♥ small effect with the range	♦	♥ crack is increased by cond.
ECP	[-150 - +100 mV]	♦ few data	♦	♥ low ECP mitigates IGSCC
Radiolytic species				
H_2	[~10ppb]	♠ high [H_2] enhances ^{60}Co release from fuel deposits	♥ high [H_2] promotes hydrogen pickup by zircaloy	♦ hydrogenation
O_2	[~200ppb]	♥ low [O_2] enhances ^{60}Co zircaloy corrosion	♥ high [O_2] promotes	♥ low ECP mitigates IGSCC
H_2O_2	[~300ppb]	♥ H_2O_2 prevent general corroison	♥ H_2O_2 promotes Zr corrosion	♥ crack is increased
Metallic species				
Fe	[~1ppb]	–	♠ thick deposits promote zircaloy corrosion	–
Cr	[~1ppb]	♥ increased pH decreases ^{60}Co release from fuel deposits	♥ higher [Cr_6^+] promotes corrosion	♥ higher [Cr_6^+] promotes IGSCC
Zn	[<1ppb]	♥ Zn moderates ^{60}Co deposition on pipes	♥ few data	♥ Zn mitigates IGSCC
Alkali metals	[<1ppb]	♠ high pH causes low ^{60}Co	♥ high [Li] promotes corrosion	♦
Radioactivity ^{60}Co, FP	[~1Bq/ml]	♠ high [^{60}Co] causes dose rate	♠ fuel defects cause high [FP]	♠ high dose rate obstructs inspection & maintenance

ECP: electrochemical corrosion potential
FP: radioactive fission products
IGSCC: intergranular stress corrosion cracking
♠ : quantified and mechanism known
♥ : quantified but mechanism not known
♣: effects of the factor known but not quantified
♦: effects of the factor not known
– small effect

Table 2. Gaps between desired information and measured data (Beyond water chemistry data).

Desired information to understand plant phenomena	Measured WC data in plants	Major measures to bridge the gaps
Corrosive conditions [H_2O_2, O_2, H_2]	• Measured [O_2], [H_2]	• Theoretical models for water radiolysis • HT O_2 sensors • ECP sensors
Crevice water chemistry	• Bulk water chemistry	• Theoretical crevice radiolysis models • Theoretical & empirical models for crack tip chemistry
Crack propagation rate	• Crack growth rate measured in auxiliary loops	• HT crack growth rate sensors • Theoretical & empirical models for crack propagation
Soluble and insoluble metallic species	• Saturated concentrations along sampling line	• Analyses of solubility & deposition/release along the lime • High temperature conductivity sensors
High temperature pH	• pH of sampled water	• Theoretical evaluation • HT pH sensors
Properties of oxide film on sampled specimens	• Characterization of oxide film	• Theoretical oxidation models • HT impedance sensors

HT: high temperature

5.2 Theoretical Models

5.2.1 Water radiolysis model for BWRs

An outline of the model is shown in **Fig. 3**. Non-linear rate equations are calculated to obtain the concentration distributions of radiolytic species throughout the primary coolant [5]. The gap between the measured ECP and effective oxygen concentration ($[O_2]_{eff}$= $[O_2]$+0.5$[H_2O_2]$) shown in **Fig. 4** [6] is explained by the contribution of H_2O_2 to ECP especially at high H_2 injection rate (**Fig. 5**) [7] .

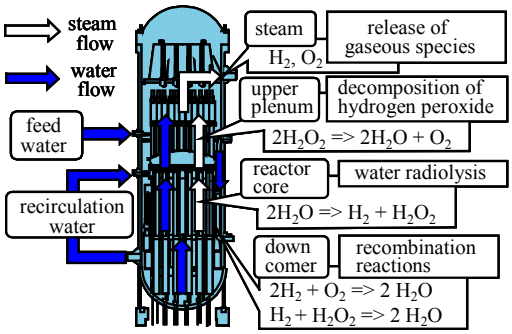

Fig. 3. Outline of water radiolysis model for BWRs.

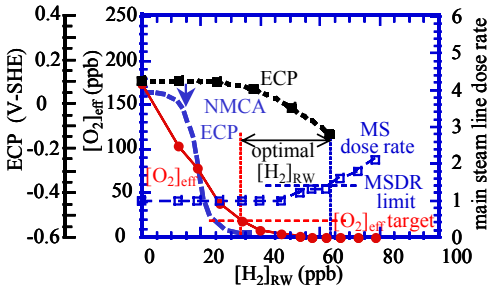

Fig. 4. Effects of H_2 injection.

5.2.2 Water radiolysis model for PWRs

In PWR primary coolant, addition of sufficient amounts of H_2 has suppressed O_2 concentration, thus avoiding problems related to corrosion.

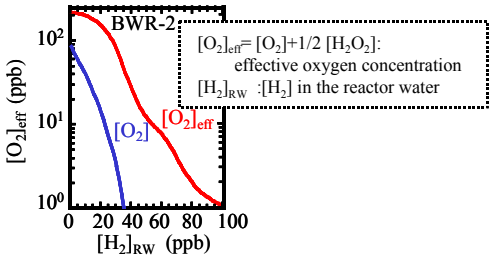

Fig. 5. O_2 and H_2O_2 concentrations in BWR coolant.

Recently, it was reported that primary water stress corrosion cracking (PWSCC) of Ni-base alloy was caused by H_2 in the coolant. In order to avoid PWSCC, optimization on H_2 concentration has necessary and a water radiolysis model for PWRs has been developed. The PWR radiolysis model is much simpler than that for BWRs because transfer of radiolytic sepecies from the water phase to the steam phase is not considered. But prior to the radiolysis calculation, high temperature pH determined by Li and B concentrations should be calculated and irradiation effects of α rays from the $^{10}B(n, \alpha)^7Li$ reaction as well as γ rays and neutrons should be considered [8]. High temperature G-values applied in the PWR radiolysis model are shown in **Table 3**.

Table 3. High temperature G-values.

species	BWR(285ºC) γ rays	BWR(285ºC) neutrons	PWR(305ºC) γ rays	PWR(305ºC) neutrons	PWR(305ºC) α rays
e^-	3.50	0.60	3.565	0.662	0.152
H	0.90	0.50	0.927	0.453	0.199
H^+	3.50	0.60	0.612	1.278	1.974
H_2	0.60	1.50	3.565	0.662	0.152
H_2O_2	0.55	1.14	0.542	0.836	1.104
HO_2	0.00	0.04	0.000	0.050	0.300
OH	4.50	1.70	4.632	1.849	1.191
OH^-	0.00	0.00	0.000	0.000	0.000

molecules or atoms / 100 ev absorption

Some results calculated with the PWR radiolysis model are summarized in **Fig. 6**. They are used to

determine $[H_2]$ needed to suppress $[O_2]$ based on data at ambient temperature, but as the recombination reaction between H_2 and O_2 is accelerated at elevated temperature, lower $[H_2]$ is expected to suppress $[O_2]$ effectively [8].

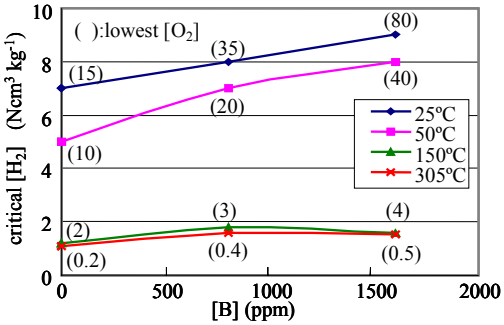

Fig. 6. Calculated results of water radiolysis model for PWRs.

5.2.3 *Crevice radiolysis model*

The concentrations of radiolytic species in a crack tip under a non-irradiation condition are too low to deduce local ECP to –600mV-SHE, while under an irradiation condition the concentrations are rather high as a result of direct species generation in the crack tip and then the local ECP is higher than that under the non irradiation condition. In order to estimate local ECP in a crack tip, a crevice radiolysis model has been developed as shown in **Fig. 7** and radiolytic species concentrations, ECP, and finally, crack growth rate have been calculated [9].

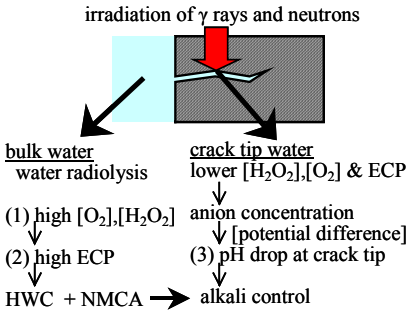

Fig. 7. Crevice radiolysis model.

5.2.4 Crevice pH model for SG tubing

One of the key issues for integrity of steam generator (SG) tubing is determination of local pH in crevices between tubing and tube support plate. Even if the SG tubing has been replaced with tubing made of corrosion resistant materials, continuous attention should be paid to intergranular attack (IGA) of tubing, especially in the crevice region. From evaluation of corrosion of SG tubing, it was concluded that both higher and lower pH values enhanced IGA. In order to prevent this IGA, pH in the SG secondary water, especially that in the crevice, should be controlled in the suitable range from pH_{300C} 5 through 10. It is not so difficult to control pH_{300C} of bulk water in the optimal range, however, control of the crevice water is hard. In order to control the crevice pH_{300C} in the optimal range, the pH_{300C} in the crevice water is calculated by using the measured concentrations of ionic species in the bulk water and their concentration factor in the crevice water obtained from mock-up experiments (**Fig. 8**) [1].

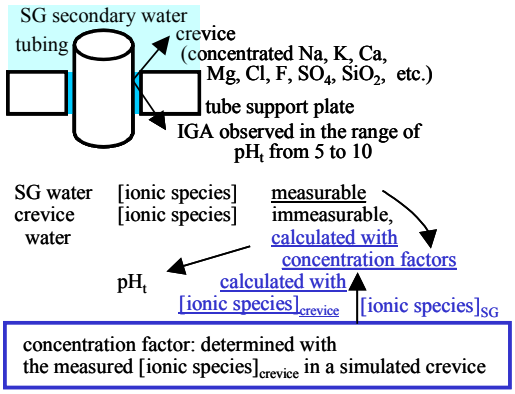

Fig. 8. Evaluation of steam generator tubing - Crevice pH_t evaluation procedures.

5.3 High Temperature Sensors

Many kinds of high temperature sensors have been developed for direct measurement of water qualities, but only a few have been applied to operating power plants [1]. **Table 4** lists high temperature sensors applied at operating plants. Most of them are sensors for structural material integrity tests. High temperature reference electrodes for ECP measurements and contact tension specimens for crack propagation measurements were applied for benchmark tests of hydrogen water chemistry in operating plants.

In order to obtain a reductive environment and thus mitigate secondary side corrosion of SG tubing, the optimum hydrazine content in the secondary system of the PWR should be discussed based on ECP measurements. However, ECP measurements will be carried out only in a very few units. Once the optimum hydrazine condition is defined, the plant staff will only routinely monitor hydrazine

Table 4. High temperature sensors for BWR water chemistry monitoring.

Plants	Power (MWe)	Reactor types	Plant utilities	Sensor location	Monitor /Test
Fugen	165	ATR	JNC	AC	ECP1, SSRT
Fukushima 1-3	784	BWR-4	TEPCO	LPRMH	ECP1, ECP2
				AC	ECP1, ECP3
Fukushima 1-5	84	BWR-4	TEPCO	BD	ECP1
				AC	ECP1, CT
Tsuruga-1	357	BWR-2	JAPC	LPRMH	ECP1, ECP2
				BD	ECP1, 2
				AC	ECP1, SSRT/CT
Tokai-2	1,100	BWR-5	JAPC	BD	ECP1, ECP2, ECP4
Shimane-1	460	BWR-3	Chugoku	BD	ECP1
KK - 7	1,356	ABWR	TEPCO	BD	ECP1 ,ECP 5

KK: Kashiwazaki Kariha ATR: advanced thermal reactor ABWR: advanced BWR
AC: autoclave BD: bottom drain LPRM: local power range monitor housing
SSRT: slow strain rate test CT: compact tension ECP: electrochemical corrosion potential ECP1: ECP(Ag/AgCl)
ECP2: ECP(Pt) ECP3: ECP(Cu/CuO_2) ECP4: ECP(Fe/Fe_3O_4) ECP5: ECP(type: not reported)

and ECP measurements can be terminated. Instead of direct ECP measurements, a combination approach of concentration measurements of anions and cations by ion chromatography and empirical calculations based on crevice concentration factors and pH evaluation has been successfully applied to determine the corrosive conditions at the tubing and the crevice between the tubing and the supporting plate [8].

6. Diagnosis Systems

Methodologies for plant diagnosis systems based on water chemistry data and expert tools have been developed in collaborative R&D programs between plant operator utilities and plant manufacturers. Combinations of data acquisition devices and computer packages have been proposed for plant applications [10]. Unfortunately, plant diagnosis systems have been applied in only restricted areas and they serve only limited purposes due to the lower predicted benefits relative to the higher facility cost and poor reliability. Much experience with the systems should be accumulated by their trial applications in plants before their regular use can be seen in the future.

7. Conclusion

In order to improve plant reliability and safety, precise and reliable evaluations of water chemistry data have been required. For this, quality assurance of the water chemistry data acquisition system is required. The quality assurance should be supported by standard procedures for water chemistry data acquisition; these are going to be established by a committee designated by the Atomic Energy Society of Japan. At the same time, theoretical models are being applied to bridge the gaps between measured water chemistry data and information desired to understand the interactions of materials and cooling water in plants. Major models already in use are:

(1) water radiolysis models for evaluating corrosive conditions in BWRs and PWRs;
(2) crevice radiolysis model for estimating crack growth rate of SCC in BWRs; and
(3) crevice pH model for evaluating corrosive conditions in crevices between SG tubing and tube support plate in PWRs.

High temperature water chemistry sensors and automatic plant diagnostic systems have been applied in only restricted areas, but they will be applied in plants after more experience is obtained with off line diagnostic systems. ECP sensors are growing in popularity as devices to determine the effects of hydrogen injection in BWR systems.

References

[1] H. Takiguchi, H. Takamatsu, S. Uchida, K. Ishigure, M. Nakagami and M. Matsui, *J. Nucl. Sci. Technol*., **41**, 214 (2004)
[2] S. Uchida, M Miki, T. Masuda, H. Nagao and K. Otoha, *ibid*., **24**, 593 (1987)
[3] K. Otoha, N. Uetake, S. Uchida, *ibid*., **34**, 948 (1997)
[4] Japanese Industrial Standards Committee, "Boiler feed water and boiler water -- Testing methods", JIS B 8224, Japanese Industrial Standard (1999) (in Japanese)
[5] E. Ibe and S. Uchida, *Nucl. Sci. Eng*., **89**, 330 (1985)
[6] S. Uchida E. Ibe, K. Nakata, M. Fuse, K. Ohsumi and Y. Takashima, *Nucl. Technol*., **110**, 250 (1995)
[7] Y. Wada, S. Uchida, M. Nakamura and K. Akamine, *J. Nucl. Sci. Technol*., **36**, 169 (1999)
[8] H. Takiguchi, M. Ullberg and S. Uchida, *ibid*., **41**, 601 (2004)
[9] T. Satoh, Y. Satoh and S.Uchida, *ibid*., **40**, 334 (2003)
[10] S. Uchida, Y. Asakura, M. Kitamura and K. Ohsumi, *ibid*., **23**, 233 (1986)