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Development of Mathematical Science in Steel Industry

Kazuto YAMAMURA*
Shinroku MATSUZAKI
Takehiko TOH
Wataru YAMADA
Junichi NAKAGAWA

1. Introduction

Since the minicomputer made its debut in the 1970s, the processing speed and memory capacity of computers have been steadily and exponentially increasing. Very recently, Japan's most advanced supercomputer "Kei" was revealed in Kobe boasting a computing speed of ten petaflops. The cost performance ratio, too, has been improving at a tenfold rate every several years. In the industrial world, more and more business enterprises are renting high-performance computers from universities or research institutes or own their own computers with speeds about one-hundredth to one-thousandth that of the above supercomputer. Steelmaking technology is characterized by these facts: (1) The macroscopic mechanical and functional properties of steel materials depend largely on the microstructures of those materials, (2) Since the manufacturing equipment is large in scale and subject to high temperatures and harsh reactions, it is difficult to conduct experiments and measurements in it, and (3) The technology is of a multi-scalar, multi-phase and multi-physical nature. Therefore, in the steel industry, the use of computers to analyze phenomena, design materials and simulate processes began relatively early (see **Fig. 1**)[1].

In this technical review, we discuss several examples of numerical analysis in steelmaking technology that has become ever more sophisticated with the development of computer hardware/software in recent years. In addition, we introduce an example of engineering applications for mathematics that Nippon Steel Corporation has been promoting as an entirely new challenge.

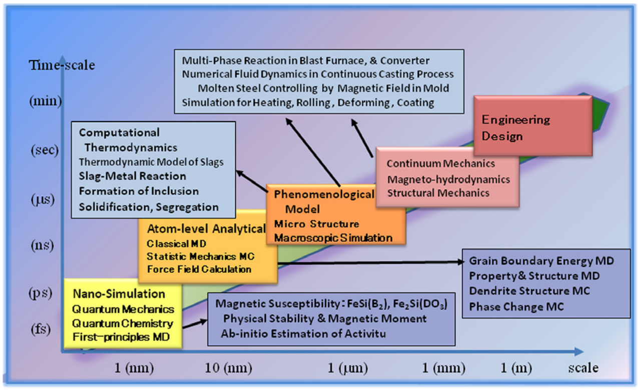

Fig. 1 Multi-scale, multi-phase, and multi-physics in steelmaking technology

2. Structural Analysis

2.1 Advances in structural analysis at Nippon Steel

Today, the finite element method (FEM) has become the most popular and most widely used technique to analyze discrete structures. FEM made its debut in the 1950s and soon developed into an approximate analysis method based on the variational principle in solid mechanics. In the late 1960s, the application of FEM was extended first to nonlinear structural problems and then to nonstructural problems. In the meantime, many types of general-purpose code were announced. Nippon Steel started applying FEM in earnest in the 1970s and introduced a general-purpose code. At present, the company takes advantage of FEM in almost all fields, from elucidating microscopic phenomena to engineering.

On the other hand, the general-purpose code alone is insufficient for solving all structural problems in steelmaking technology, which has many unique characteristics as mentioned in the preceding section. Therefore, we have developed and applied phenomenon-oriented mathematical models that relate specific phenomena in processes to specific equipment.

We introduce below several examples of the application of numerical structural analysis techniques which help to clarify the mechanisms of phenomena governing the damage, deterioration and functional limits of structures, or propose seeds for new processes and equipment to implement those new processes as well as optimizing those processes and equipment.

2.2 Technology for analyzing brickwork structures (discontinuous structures)

In the iron and steel industry, many structures are made of refractories (bricks and monolithic), mainly for high-temperature processes. In particular, for those problems which involve contact between many bodies, as in brickwork structures, there is a very strong need to elucidate the mechanisms of damage, such as joint opening, ratcheting, cracking and collapsing, and for optimum design of structures (shape and method of brickwork, joint/dowel structure, etc.), and heat transfer mechanisms, etc. to prevent such damage.

Analyzing such discontinuous structures as mentioned above is a sphere of solid mechanics which requires extremely complicated calculations. Therefore, various analytical techniques have been proposed and applied to solve or evaluate actual problems with those structures.

On the basis of the rigid bodies-spring model (RBSM)[2] developed by Kawai et al., Nippon Steel has come up with the brickwork structure analytical program, NS-Brick, which takes into account the characteristics of joints and dowels unique to brick. NS-Brick is a

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* Chief Researcher, Process Engineering Div., Process Technology Center
20-1, Shintomi, Futtsu, Chiba 293-8511

generalized discrete limit analysis technique based on the infinitesimal deformation theory. It assumes the individual elements to be rigid bodies and uses a spring provided on the boundary between the elements to evaluate the energy of the surface force, rather than the work done inside the element. Thus, it allows for efficient limit analysis taking into consideration any slip as well.

As an example of the analytical technique being applied, we clarified the unwanted phenomenon of brick rise, which can damage the lower tank in vacuum degassing equipment (RH), in our study of the optimum brickwork structure to prolong tank life (see **Fig. 2**).

Incidentally, since this technique treats the individual elements as rigid bodies, it cannot be used to grasp the strain and stress conditions inside the elements. Thus, when it comes to handling the deformation of a structure or the propagation of a crack in the structure, the analytical technique has its limits. In evaluating the critical yield strength of a brickwork structure, the partial fracture and deformation of the structure preceding its collapse becomes a problem. With RBSM, however, the behavior of the brickwork structure cannot be evaluated accurately.

Therefore, on the basis of the principle of virtual work taking into account not only the displacement method but also the stress method, we developed a new brickwork structure analysis program, NS-Brick II, using the hybrid-type penalty method (HPM) developed by Takeuchi et al.[3] HPM performs a discrete limit analysis assuming the presence of a linear displacement field. With the rigid-body displacement and strain as parameters, NS-Brick II has introduced the same concept as the spring in RBSM and uses the penalty function as the spring constant, since Lagrange multiplier physically refers to the surface force.

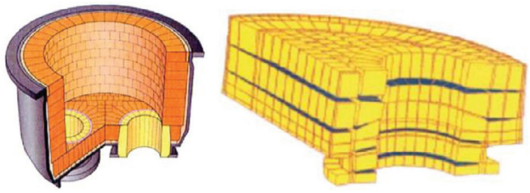
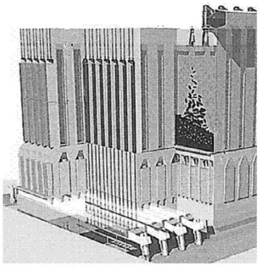
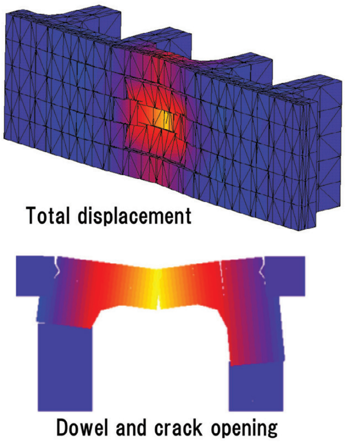
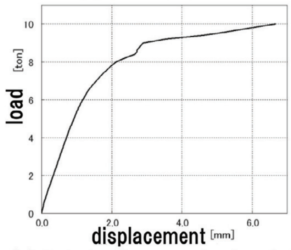

(a) RH Structure (b)Uplift of brickwork

Fig. 2 Example of NS-Brick (RBSM)


(a) Coke oven



(b) Total and partial displacement



(c) Relation between load and displacement

Fig. 3 Example of New NS-Brick (HPM)

Fig. 3 shows an example in which this technique was used to estimate the fracture load for the brick walls of a coke oven. Fig. 3 (b) shows the general deformation and the occurrence of joint opening and cracking in the horizontal section passing through the point of loading when a load was applied to the center of the brick, and Fig. 3 (c) shows the load-displacement curve, which indicates that the brick wall strength declines with the increase in applied load.

2.3 Technology for analyzing thermal-mechanical behavior of solidifying shell in continuous casting

In the continuous casting process, understanding the growth behavior of the solidifying shell (the part of the molten steel that solidifies into the solid phase) is of paramount importance from the standpoint of achieving the highest possible stability and productivity of the process. Most conventional analyses of solidifying shell behavior employ the non-steady method in which the system of coordinates is fixed to the unit intercept of the slab.[4] This method permits calculating the temperature and stress while changing the surrounding boundary conditions on a time-serial basis. However, it neglects the temperature gradient and stress gradient in the casting direction.

In view of the above problem, a method which takes viscoplastic behavior into consideration and which analyzes the solidifying shell behavior in the velocity field under the space-fixed system of coordinates as in the rigid-plastic analysis of rolling was proposed.[5] However, since the model was a two-dimensional one which assumed the generalized plane strain, it was insufficient for expressing the cracks and suchlike that occur in actual slabs. Therefore, focusing on the fact that the thickness of the solidifying shell in the mold is sufficiently small relative to the size of the slab and that the temperature distribution in the shell thickness direction can be expressed by a comparatively simple curve, we developed a three-dimensional finite element analysis model which takes into account the phase transformation, thermal shrinkage and viscoplastic behavior, including the mass transfer and solidification, through formulation using the shell elements. The procedure for these calculations is shown in **Fig. 4**.

Using the solidifying shell distortion analysis model mentioned above, we analyzed the influence of the mold shape on molten steel solidification in order to optimize the mold shape; specifically the shape of the taper (inclination) of the narrow face of the mold. The condition for formation of the gap (void or space filled with powder inflow) between the solidifying shell and the narrow face copper plate differs according to the shape of the narrow-face side taper. As shown in **Fig. 5** (b), with the narrow face having a single-stage taper, on the right, the amount of the initial thermal shrinkage of the slab becomes larger than the amount of the taper, producing a large gap

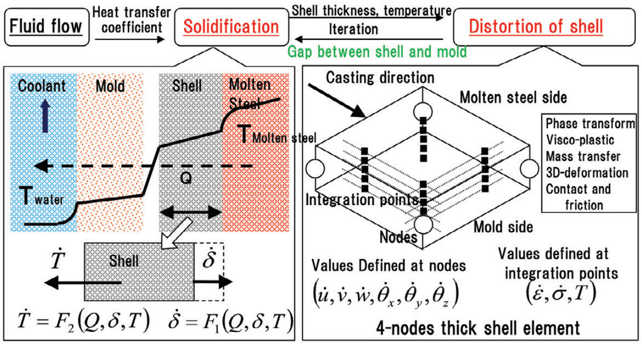
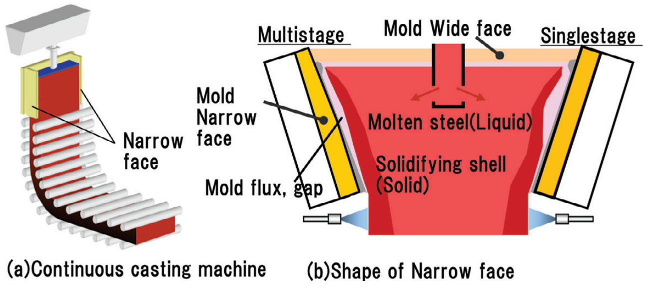


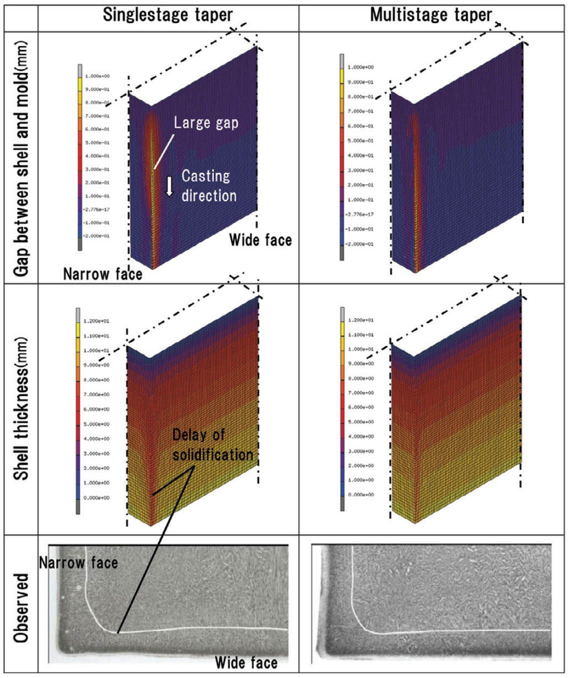
Fig. 4 Thermal-mechanical model for solidifying shell



(a)Continuous casting machine (b)Shape of Narrow face

Fig. 5 Shape of mold narrow face and distortion of solidifying shell

Table.1 Evaluation of multistage taper effect



between the shell and the mold. As a result, solidification of the molten steel near the corners is delayed and the shell at the bottom of the mold remains thin. In this case, cracks and breakout (the problem of the shell breaking and then leaking molten steel) tend to occur easily. In order to resolve the above problem, a mold narrow face with a multistage taper was proposed and put to practical use. Fig. 5 (b) shows a narrow face with a multistage taper on the left. The upper taper is larger than the lower taper. Because of this, the amount of taper is closer to the amount of thermal shrinkage due to the initial solidification and the formation of a gap is restrained. As a result, any delay in solidification is less likely.

Table 1 shows an example of quantitative evaluation of the influence of the taper shape on growth of the solidifying shell, carried out using the developed model. It was confirmed by calculations and measurements that the application of a multistage taper reduced the gap near the corners and facilitated uniform solidification. Accordingly, we could confirm the practicality of our model. Therefore, we designed the optimum taper shape and applied it to existing equipment. As a result, the uniformity of the solidifying shell's thickness near the corners improved, allowing for more stable and faster continuous casting.

2.4 Dynamic structural analysis for stable threading of strip

In the continuous annealing line for strip and the continuous processing equipment for pickling, surface treatment, etc., stable strip threading technology to ensure a high product quality and high productivity has become important in view of the diversification of products (e.g., wider, thinner or softer steel products) and increasingly exacting demands for product quality from users.

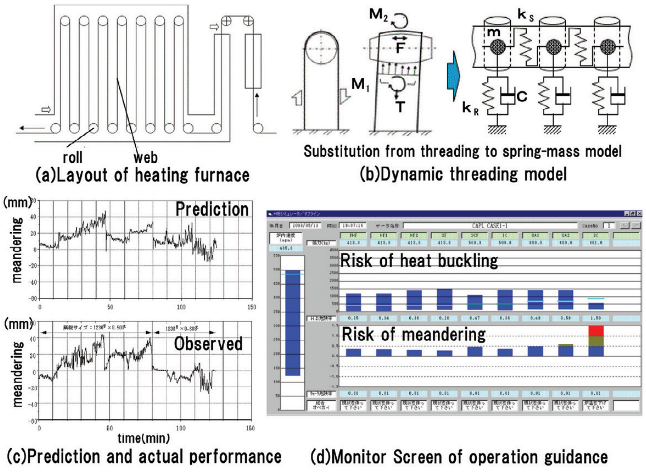
Typically, in the above continuous processing equipment, the strip passes through the reheating furnace, various types of cooling equipment, and pickling/plating tank while moving on or between rolls. In that process, the strip is subject to various influences, including its contact with rolls, thermal history, fluid force of gas/liquid, and electromagnetic force. As a result, shape defects (transversal bends, wavy edges, creases (buckles), etc.) and unwanted phenomena (meandering, fluttering, etc.) can affect the strip.

With the aim of clarifying those mechanisms and optimizing the equipment, Nippon Steel has developed a dynamic model which permits studying the continuous processing lines in a unified and time-sequential manner.

Generally speaking, rolls on the continuous processing line, especially those in the reheating furnace, are provided with a crown to prevent the strip from meandering due to its reeling effect (the roll radius is larger at the center than at either end). Depending on the strip tension and temperature, however, creases can occur on the strip. Therefore, the roll crown calls for optimum design.

Fig. 6 shows a meandering model and an example in which it is used to predict the meandering of strip and provide on-line guidance to thread the strip. The meandering model expresses the threading system as equivalent to a spring-dashpot system since the relationship between the threading speed and the strip transfer speed across the roll width is a primary delay system. With the system shown above, it is possible to predict the threshold for creasing, too, on the basis of the buckling theory.[6)] The system is also used to implement optimum design of roll crowns.

As an example of a strip-threading model that is subject to a fluid force, the continuous hot-dip galvanizing process is discussed below. In this process, the strip is first passed through a molten zinc bath to cause molten zinc to deposit on the strip surfaces. Then, the redundant molten zinc is removed from the strip (wiping) by jets of air from nozzles installed over the bath to adjust the coating thickness.



(a)Layout of heating furnace (b)Dynamic threading model

(c)Prediction and actual performance (d)Monitor Screen of operation guidance

Fig. 6 Dynamic threading model and application

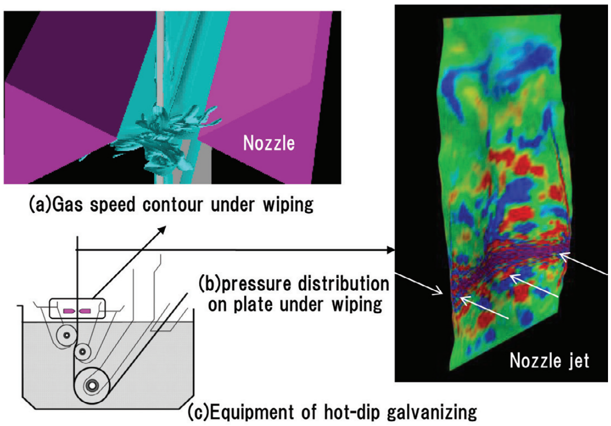


Fig. 7 Example of wiping analysis in the hot-dip galvanizing line

Fig. 7 shows an example of analysis of this wiping. Physically, wiping is the phenomenon of fluid-structure interaction; that is, excitation of the strip accompanying opposite impinging flows at the strip edge. It is also the phenomenon of a violent two-phase flow whereby a thin liquid film formed on the strip surface is scraped off by jets of air. With the aim of clarifying the mechanisms of those phenomena, we are deepening our quantitative understanding of wiping by analyzing the fluid-structure interaction. On the basis of the results of our analyses, we optimize the construction of nozzles and the arrangement of rolls, etc.

2.5 Outlook for future structural analysis

From the standpoint of optimizing both the steelmaking processes and equipment, it is expected that the need to respond to complicated problems involved in multi-physical, multi-phase, multi-scalar and multi-body steelmaking technology will increase further in the future. Macroscopically, we consider that structural analysis will evolve in two directions in the future—techniques based on the particle method, and techniques based on continuum mechanics. The former techniques are represented by SPH and PFEM, and the latter by HPM and XFEM. Since all those techniques have both merits and demerits in terms of computer load and analytical accuracy, it is extremely important to select the optimum technique in accordance with the purpose. Nippon Steel intends to continue its research and development on practical, purpose-oriented mathematical models.

3. Fluid Analysis

3.1 DEM models of blast furnaces

The blast furnace is a "reactor" for producing iron from a mixture of iron ore and coke (burden) put into it from its top. The burden is processed as follows. The coke is burned by blasts of hot air (at about 1,200℃) from multiple nozzles (tuyeres) installed in the lower part of the furnace, and the iron ore is heated, reduced and melted by the high-temperature reducing gas (mainly gaseous CO) generated from the coke. The reducing gas whose temperature is as high as about 2,000℃ is sent out from the tuyeres and reduces the iron ore while heating the burden. Eventually, the gas is exhausted from the furnace top as its temperature decreases to about 200℃. The efficiency of heat exchange and reduction in the furnace is influenced not only by the way the burden is charged but also by the condition of the charged burden itself. On the other hand, the condition of the charged burden in the upper part (lumpy zone) of the furnace is determined by such physical properties as grain size distribution and bulk density, whereas in the lower part of the furnace it is influenced largely by the conditions of the cohesion zone and deadman.

Therefore, in order to make the most of the blast furnace functions, it is important to maximize the efficiency of heat exchange and reduction in the furnace by letting the hot gas rise effectively from the lower part of the furnace upward and to make the powder descend smoothly to the lower part of the furnace. This also helps to reduce the consumption of carbon as a reducing agent in the blast furnace. Needless to say, in order to achieve the purposes mentioned above, it is important to clarify the flow mechanisms of solids and gas in the blast furnace. Today, therefore, models for handling them in a distinct manner have become more popular than conventional continuum models.

Under those conditions, Nippon Steel has developed solid flow models based on the distinct element method (DEM)[7, 8]. Concerning the burden distribution, the company has come up with a one-dimensional DEM model mainly for analyzing the segregations in the blast furnace and two- and three-dimensional DEM models mainly for handling the charging of raw materials and fuels into the blast furnace. In order to estimate the conditions in the blast furnace interior, Nippon Steel has developed a three-dimensional DEM model jointly with Kyushu Institute of Technology.

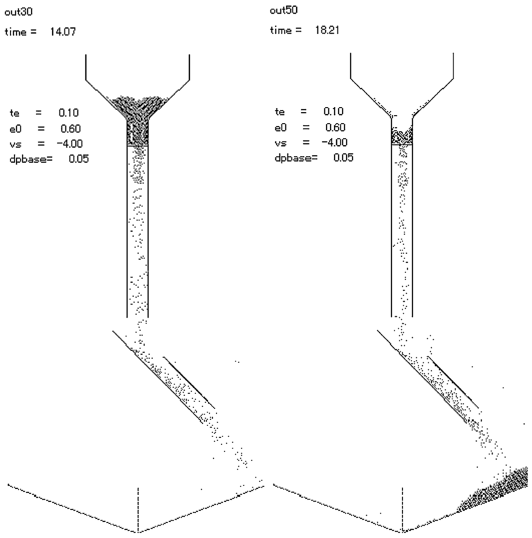
3.2 DEM model of burden distribution

Fig. 8 shows the results of a simulation of bell-less charging equipment obtained by using a DEM model at the early stage of development.[9] Due at least in part to the inadequate capacity of the computer system used, we could only handle thousands of particles, with the turning of the chute left out of consideration.

After that, the model was expanded into a three-dimensional one. The current model almost meets the specifications of an actual blast furnace, from the surge hopper to the charging equipment (see **Fig. 9**).[10] Verification of the model has also been carried on using a large, one third-scale experimental apparatus.

3.3 Models of gas/solid flows in blast furnaces

Concerning the gas/solid flows in the blast furnace too, we have pursued the development of models, starting with a two-dimensional one. **Fig.10** shows the behavior of particles near the raceway calculated two-dimensionally.[11]



a) 300000step b) 500000step

Fig. 8 Calculation example of deposition and discharging process of burden to the hopper by two-dimensional DEM model[9]

Figs. 11[12] and **12** show examples of the results of our attempt to measure the fluctuations in solid/gas flows in the blast furnace by calculating the void ratio and differential pressure distributions when scaffolding or bridging occurs in the blast furnace.

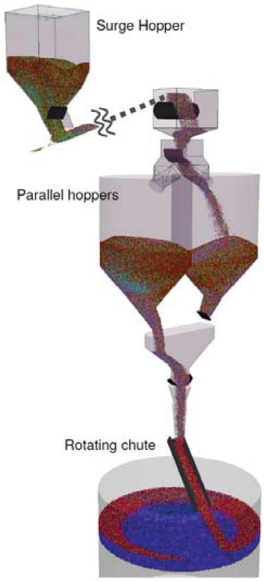


Fig. 9 Calculation example of deposition and discharging process of burden to the hopper by three-dimensional DEM model[10]

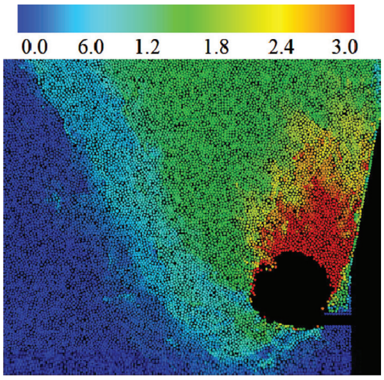
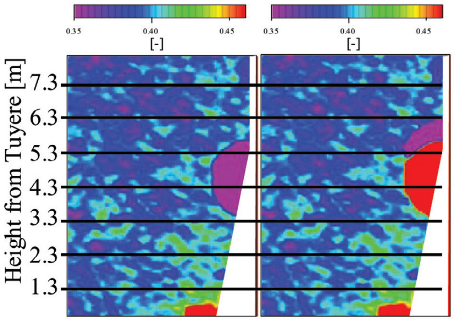


Fig.10 Packed status and velocity of coke in the neighborhood of raceway[11]



a) scaffold b) Hanging

Fig.11 Distribution of void fraction[12]

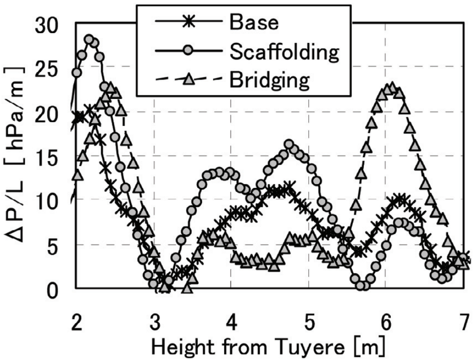


Fig.12 Differential pressure distribution in the furnace wall

3.4 DEM model utilizing earth simulator[13, 14]

DEM models are becoming a very powerful tool for analyzing the flow of solids. On the other hand, since they judge the behavior (contact, etc.) of each of the particles involved, the computing time increases exponentially with the increase in the number of those particles. With the aim of solving that problem, we conducted studies for the development of larger and faster models using the so-called earth simulator owned by the Japan Agency for Marine-Earth Science and Technology (JAMSTEC), which is an independent administrative institution.

With a model which simulates an actual blast furnace in the 5,000 m^3 class, we arranged layers of coke and iron ore in a region occupying one-quarter (90 degrees) of the circumference and the entire height, injected air into the region from ten tuyeres at a speed of 250 m/s when the burden began to descend, and thereby simulated the heterogeneous multiphase flow that is generated in the actual blast furnace by the mutual interference with the particles descending in the form of a layer. The model had 16 nodes and about three million points of contact for the air current calculations. The number of particles calculated was about twelve million.

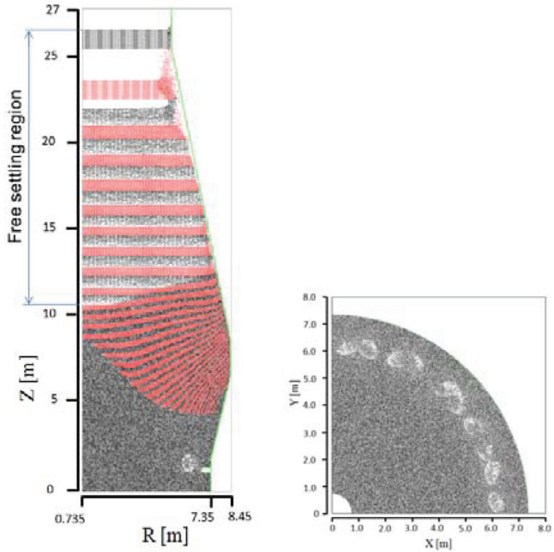
The calculation results are shown in **Figs. 13** and **14**. It can be seen that we are better able to calculate the condition of particle packing and the gas-solid flows in an actual blast furnace.

Speeding up these DEM models is a task to be tackled in the future.

The DEM-based blast furnace models developed by Nippon Steel are now producing tangible results. However, in order to estimate or predict the interior conditions of actual blast furnaces using a DEM model, it is necessary to simulate as many as hundreds of millions of particles. In this respect, we consider it indispensable to increase the scale and speed of the calculations.

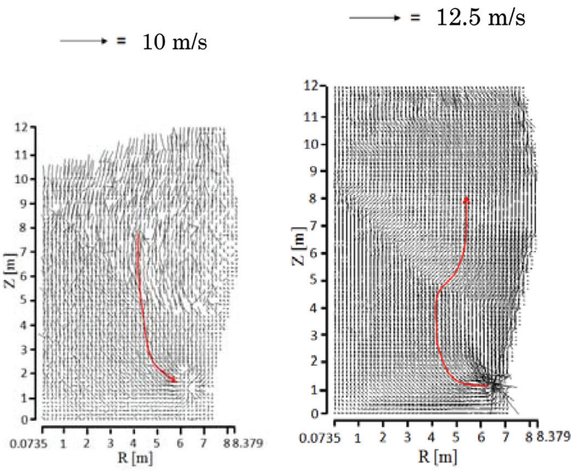
3.5 Numerical analysis of multiscale, multiphysics phenomena in the continuous casting process

In terms of space-time, the continuous casting process is a multiscale process: the typical process length being several meters; solidification structure, several μm to hundreds of μm; nonmetallic inclusions/air bubbles, several μm to several mm; time scale, tens of minutes to several hours; solidification time, several milliseconds. It is also a multi-physical process: the wide range of flows, from laminar flows to turbulent flows with the Re number up to hundreds of thousands; advective diffusion of heat and solutes; mixed-phase flows of gas, slag and metal; free interfaces and moving interfaces; chemical reactions and solidification; transformation and other phase changes; formation, advective diffusion and cohesion aggregation of nonmetallic inclusions; flow control using an electromagnetic field



a) Vertical cross-sectional view b) Horizontal sectional view

Fig.13 Particle position at T = 2.37s



a) Solid flow b) Gas flow

Fig.14 Velocity vector at T = 2.37s

and the magneto-hydrodynamic phenomenon accompanying plasma heating, etc. as well as elastic-plastic creeping of slab; etc. Although it is difficult to understand those problems completely, it has become possible to grasp the various phenomena involved in them in a quasi-steady way. Below, we describe our technology for simulating the flow of molten steel and the behavior of nonmetallic inclusions/air bubbles in sequential casting and introduce an example of application of the technology.

(1) Object of analysis

The ladle that contains secondary-refined molten steel is transferred to the continuous casting process, in which it is replaced with the succeeding ladle by the turret. In the meantime, the continuous casting operation proceeds and the level of molten steel in the tundish that supplies molten steel to the molds drops while changing the ladles. As the hole in the succeeding ladle is opened, the molten steel surface rises to the prescribed level and the molten steel reaches a quasi-steady state. The phenomenon that takes place during this process is an extremely complicated one accompanying a free surface and mixed-phase flow. Speaking of the qualities of nonmetallic inclusions in molten steel, throughout the continuous casting operation, alumina-based nonmetallic inclusions which float in the ladle continue flowing into the tundish. At the end of the operation of the preceding ladle, a layer of molten slag formed at the molten steel surface flows into the tundish, together with the molten steel, thereby forming slag-based nonmetallic inclusions. These nonmetallic inclusions are partly reduced into alumina-based nonmetallic inclusions by aluminum contained in the steel. In particular, alumina-based nonmetallic inclusions several μm in diameter coagulate into clusters. Clusters tens of μm and more are especially harmful. (For details about the techniques to analyze nonmetallic inclusions, see References 15 through 19.)

(2) Analytical results

Fig.15 shows an example of analysis of molten steel flow and temperature by our coupled model. **Fig.16** shows the concentration distributions of alumina-based nonmetallic inclusions after the change of ladles for inclusion sizes 1 μm and 100 μm. This figure expresses the increase in concentration of 1-μm nonmetallic inclusions due to the re-oxidation of steel in the above-mentioned tundish and the increase in concentration of 100-μm nonmetallic inclusions due to the coagulation of smaller particles. In order to minimize the concentration of nonmetallic inclusions in the ladle change unit, efforts have been made to reduce the amount of slag outflow from the ladle, adjust the level of molten steel in the tundish, and so on. Nevertheless, the inflow of nonmetallic inclusions into the mold cannot be completely prevented. In this respect, the floatation of nonmetallic inclusions in the mold is also an important technology. The level magnetic field (LMF) is a technique used to float nonmetallic inclusions in the mold.[20)]

In LMF, a direct current (DC) magnetic field which is uniform across the casting width is applied to the nozzle outlet for injection of molten steel into the mold in the direction of the mold thickness so as to generate an electromagnetic force opposite in direction to the flow of the injected molten steel to lower the flow rate of the molten steel, thereby preventing the molten steel from flowing deep into the continuous casting strand. Thus, LMF helps to float nonme-

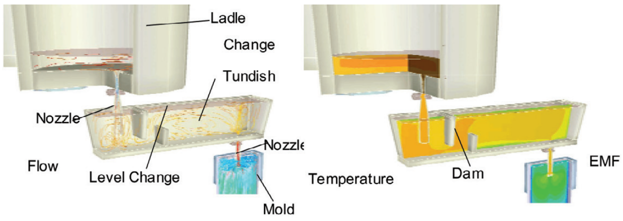
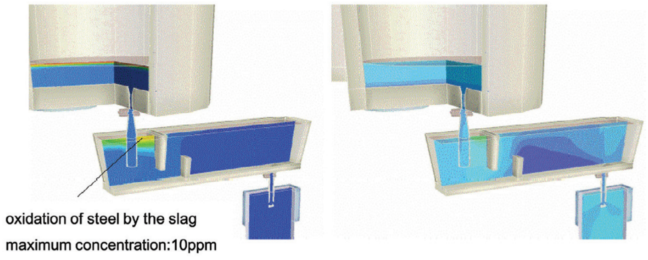


Fig.15 Flow and temperature field just before the ladle change



inclusions 1μm in diameter inclusions 100μm in diameter

Fig.16 Concentration distribution of nonmetallic inclusions just before the ladle change

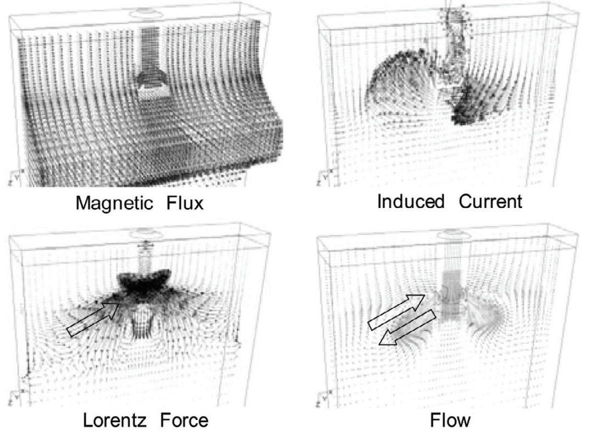


Fig.17 Results of magnetohydrodynamic analysis in CC mold with electromagnetic braking technology LMF (level magnetic filed)

tallic inclusions of molten steel in the mold. **Fig.17** shows the results of an analysis coupled with the potential method mentioned earlier. The results shown are the magnetic flux density, induced current and electromagnetic force distribution when the level magnetic field was applied.[21] By applying this technique, it is possible to restrain the occurrence of defects due to nonmetallic inclusions and improve the productivity of continuous casting. It should be noted that when the level magnetic field is used, the behavior of solidification of the molten steel through the flow field changes and the deformation of the slab inside the mold is expected to change as well. Through a deformation-coupled analysis applying the finite volume method,[22] it has been demonstrated that LMF helps homogenize the solidification shell in the mold circumferential direction and flatten the slab.[23]

(3) Future of molten steel flow analysis

By developing a multi-scalar, multi-physical analytical technique based on the finite volume method, Nippon Steel has made it possible to analyze the quasi-steady flow of molten steel and the time-serial changes in various physical and chemical properties of molten steel in the sequential casting operation. This in turn has made it possible to evaluate the quality behavior of non-steady portions of molten steel and estimate the effects of any improvement measures taken. As future research themes, it is expected that advances in high-performance computing technology will be fully utilized to apply precise models of free surfaces and mixed-phase flows which demand extremely small increments of time and to implement microscopic analyses with models which permit obtaining directly and digitally those boundary conditions which have been empirically derived from limited amounts of sampling data and analytical theories but which are difficult to measure accurately, such as the formation of slag-based nonmetallic inclusions by entrapment of ladle slag and the particle distribution of argon gas bubbles produced inside the nozzle.[24] In addition, since continuous casting is a system in which the flow of solids, the formation of solidification structures and the deformation of slabs interact in a complicated manner, developing a fast, dependable coupled-analysis technique can be cited as another task to tackle in the future.

4. Micro-scale Computational Materials Science

4.1 Application of micro-scale computational materials science at Nippon Steel

The microscopic mechanical and functional properties of steel materials depend substantially on their microstructure. In the design of a steel material, the alloy phase diagram plays an important role as a “map” which provides guidelines on the optimum alloy composition and process conditions for obtaining the sought-for microstructure. Paying attention early on to CALPHAD (CALculation of PHAse Diagram), Nippon Steel has introduced a number of computer programs for thermodynamic equilibrium analysis, such as SOLGASMIX[25] and Thermo-Calc,[26] as well as thermodynamic databases, and has applied them to the analyses of practical materials and actual processes.[27] In addition, Nippon Steel has pressed ahead with what it calls “computational thermodynamics,” which simulates thermodynamic phenomena and processes in themselves by coupling the kinetics of solute element diffusion/segregation or refining chemical reactions with local equilibrium analysis.[27]

On the other hand, in order to respond positively to the increasingly strict demand for steel material properties in recent years, it has become more important than ever before to understand the basic characteristics of materials by means of electron-level microscopic analyses.

At present, we intend to meet the above needs by applying to the analysis of steel materials the electron-level “first-principles computational analytical technique” that has been improving in terms of quantifiability and reliability with the enhancement of computer performance. In the future, we would like to develop a new multi-scale computational materials science technique that combines the above analytical technique with an atom- or meso-level analytical technique to permit analyzing both microscopic and macroscopic characteristics. We believe that establishment of the calculation technique leads to deeper understanding of the characteristics of materials if effectively combined with experimental research. In the following subsection, we introduce a couple of examples of the microscopic analysis mentioned above

4.2 Introduction of technology for microscopic simulation of materials

(1) Simulation of electronic/atomic structures of steel materials

The first example is a technique to predict the concentration of hydrogen in crystal grain boundaries by means of first-principles calculations. In recent years, there is an ever-increasing demand for steel materials of higher strength. On the other hand, in the case of high-strength steels, such as the ultrahigh-tensile steel for automotive sheet exceeding 1 GPa in tensile strength, hydrogen embrittlement is a major obstacle in the path of further expansion of their applications. Removing this obstacle calls for a technology which permits comprehending and controlling the amount of hydrogen captured in the steel grain boundaries, since this has much to do with the embrittlement of the steel. The hydrogen that has entered the steel is captured not only in the grain boundaries but also in lattice defects (e.g., dislocations and atomic vacancies), precipitates of carbides, etc. Besides, the rate of hydrogen diffusion is very high. For those reasons, it was difficult to accurately predict the amount of hydrogen captured in the grain boundaries of steel. As part of the national project named “Development of Prediction Technology/Techniques to Clarify the Mechanism of Low-Temperature Cracking of Joints of 980-MPa Class by Entry of Hydrogen and to Secure Adequate Reliability of Those Joints,”[28] we have developed a technology to quantitatively predict the hydrogen captured in the grain boundaries of steel with the aid of models we created to evaluate the hydrogen-capturing energy at various defects in the steel, including the grain boundaries in α-iron, on the basis of first-principles calculations and experiments, and to calculate the diffusion of hydrogen in α-iron and the dynamic behavior of the phenomenon whereby hydrogen is captured in various defects.

Fig. 18 shows the calculation results for the hydrogen capturing energy at various sites in a TiC coherent precipitate in α-iron. Contrary to our previous assumptions, the results show that the hydrogen-capturing energy at the coherent interface and carbon vacancies in TiC is greater than that in the coherent strain field. As a matter of fact, it has been confirmed by observations using a three-dimensional atom probe (3D-AP) that the capturing of hydrogen at the coherent interface is predominant.[29] With respect to the hydrogen-capturing energies calculated for VC and cementite too, they agree well with such experimental data in terms of their thermal desorption spectrum (TDS). On the assumption that hydrogen (2 ppm) entered α-iron having a crystal grain size of 10 μm and containing a high density of dislocations ($10^{15}/m^2$), we calculated the final amount of hydrogen at each defect point on the basis of the above calculation results, etc. The calculation results are shown in **Fig.19**. The implication is that if we can quantitatively grasp the amount of hydrogen at the crystal grain boundaries that has been difficult to evaluate even experimentally, it should become possible to predict the presence or absence of hydrogen embrittlement by comparing that amount of hydrogen with the critical hydrogen concentration to crack initiation that can be obtained by experimentation. The technique to predict the hydrogen concentration in crystal grain boundaries that has been described so far may be said to be a good example of the multi-scale analysis that began with a microscopic analysis and led to the prediction of hydrogen embrittlement—a macroscopic characteristic of steel.

As another example in which one of the essential characteristics of steel was understood from first-principles calculations, the results of our simulation of the influence of the segregation of sulfur (S) on the strength of γ-grain boundaries are described below. The intergranular segregation of S causes the grain boundary strength to decline markedly and induces cracking of the steel in the casting and hot working processes. It has been known that in a steel with Ni added, which is an element often used to improve the low-temperature toughness of base metal, the phenomenon of intergranular embrittlement by S is promoted.[30] With the aim of understanding the basic cause of intergranular embrittlement of Ni-added steel by S, we analyzed the intergranular strength of steel with and without Ni addition by first-principles calculations with a focus on the interatomic binding force of S.

Considering a model structure in which Ni and S coexist in grain boundary Σ 9 (221) [110] in γ-iron as shown in **Fig.20**, we calculated the binding energy when the grain boundary was separated and compared the calculated energy with the energy in the absence of Ni. As shown in **Fig.21**, it was found that when Ni and S coexist, the energy required to form a surface with the grain boundary separated is smaller. Thus, the calculated result coincided with the actual experimentally obtained phenomenon in which the coexistence of Ni and S in the grain boundaries promotes the intergranular cracking of steel. From a detailed analysis of the electronic structure, we understood the cause of intergranular embrittlement to be as follows. Essentially, as the 3p electronic state that corresponds to the anti-bonding orbit of S atoms, was occupied by the Ni addition, the S atoms repelled one another and thereby their binding force was weakened.

The two examples described above are those of analysis of a phenomenon caused by intergranular segregation. Various phenomena relating to grain boundaries are difficult to analyze by experimentation. Therefore, we consider that they will remain a promising field in which microscopic calculation techniques, including electronic structure analysis, play a vital role. In addition to the above examples, we have attempted to calculate various physical properties of steel, such as the interaction energy of solute and the formation energy for precipitate. By using those physical properties as part of the thermo-

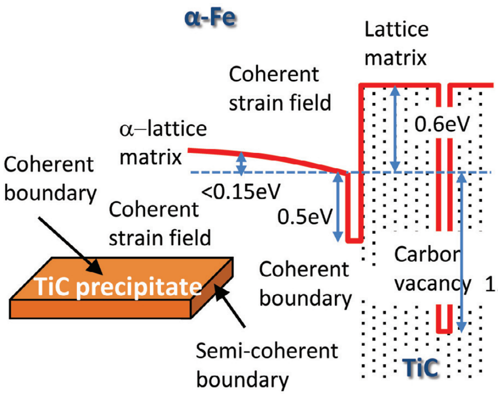


Fig.18 Hydrogen trapping energy at TiC precipitate in α -iron

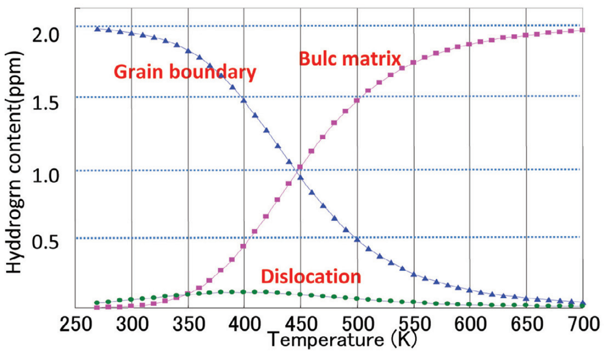


Fig.19 Calculated hydrogen distribution in α -iron

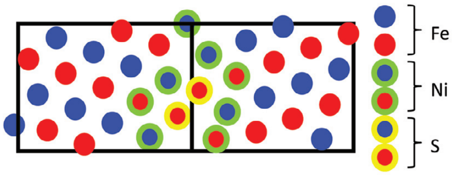


Fig.20 Atomic structure model for grain boundary co-segregation of Ni and S atoms in γ iron

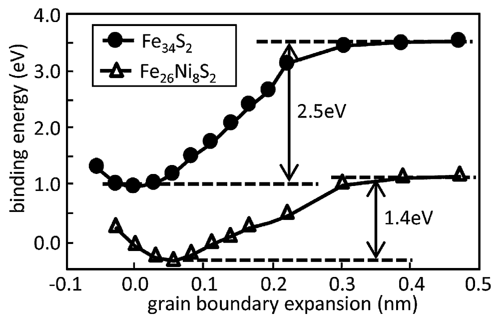


Fig.21 Binding energy change by separation of the grain boundary for $Fe_{34}S_2$ and $Fe_{26}Ni_8S_2$
The cohesive energy for each case is shown.

dynamic data for meso-level structural analysis simulations and phase analyses by CALPHAD, we are expanding the application scope of multi-scale computational materials science.

(2) Application of quantum chemical simulations to the study of environmental problems

Identifying, decomposing and removing environmental pollutants generated from factories, removing greenhouse gases, searching for new energy sources as substitutes for fossil fuels… many of these technical activities to solve environmental problems are challenges of a chemical nature. Computational chemistry is a generic term for simulation techniques applicable to atoms, molecules and nano-scale substances. Thanks to the remarkable improvement in computer performance in recent years, it has become an indispensable tool in the fields of chemistry, pharmacy, and electronics, etc. Of computational chemical techniques, calculations based on quantum mechanics are called quantum chemical simulations. We are active in promoting the application of quantum chemical simulations to solve various environmental problems.

Recently, CO_2 Capture and Storage (CCS) has attracted attention as a promising technology for coping with global warming. In large processes for separation and recovery of CO_2 from blast furnace gases at steelworks or from combustion gases at power stations, there is a good possibility that a chemical absorption technique using amine solution as the absorbent will be put to practical use. In this particular field too, several research institutes have been analyzing the mechanisms of various reactions involved in CCS by means of quantum chemical calculations. Since those reactions take place in a solution, giving due consideration to the effect of the solvent used is the key to accurate analysis.

We are tackling the same task using a computational technique which takes into account the polarization effect of solvent measured with a dielectric continuum model within the framework of the density functional theory.[31] **Fig.22** shows an example in which the above technique was used to analyze the reaction whereby monoethanolamine combines with CO_2 to produce a carbamate anion. The molecular structures of reactants, transition states (TS1, TS2), intermediates, and products on the reaction path and the corresponding potential energies are shown. By comparing the energy in the gas phase and the energy in water in the diagram, it can be seen that the reaction is strongly influenced by the solvent. In particular, the solvation stabilizes TS2 so much that the activation energy at the second stage decreases markedly. As a result, in the water, the reaction at the first stage becomes the rate-determining step. This result agrees with the suggestion from experimental results. At present, we apply the above reaction calculations to develop high-performance CO_2 absorbents.

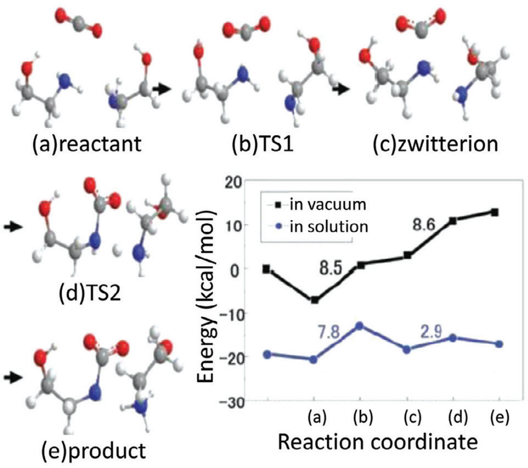


Fig. 22 Energy profiles along CO_2 absorption reaction in monoethanol amine aqueous solution (the values indicate activation energies)

In technical activities to deal with environmental problems, mainly those of a chemical nature, the role of techniques to analyze/predict molecular properties and chemical reactions by quantum chemical calculations is expected to become increasingly important in the future. We, too, would like to help solve environmental problems and realize a sustainable society with the aid of the most advanced theories of quantum chemistry.

5. Technology for Mathematical Engineering Applications

The steelmaking process involves extremely complicated manufacturing conditions. For example, it handles various types of solids, liquids and gases under varying conditions, from normal temperature and pressure to extremely high temperatures and pressures. Quite a few of the phenomena that occur there have been controlled according to the empirical rules established by field workers or the tacit knowledge derived from data obtained in the past. Under those conditions, Nippon Steel found it possible to gain a basic understanding of those phenomena that are based on fundamental principles by utilizing mathematics. Since then, the company has been seeking and evolving new forms of industrial-academic cooperation to concentrate the wisdom of mathematicians and steel researchers. Taking advantage of our traditional engineering-based R&D style reinforced with mathematics, which provides an entirely new means of expressing phenomena, we have been tackling diverse problems we encounter in the course of steelmaking (**Fig.23**).

For example, **Fig.24** shows an example of analysis of inverse problems on the heat transfer of brickwork at the bottom of a blast furnace. Inverse problem solving is a mathematical technique to identify the basic cause or factor of a phenomenon which cannot be directly measured from the results of indirect observation of the phenomenon. In this example, we developed a technique to calculate back, with the aid of an equation of heat conduction, the internal temperature and heat transfer coefficient of the brickwork (which were generally difficult to measure directly) from the results of temperature measurement by thermocouples embedded in the brickwork. With this technology, we found for the first time that the temperature inside the furnace was frequently going up and down right before the refractory temperature sharply rose abnormally. By visualizing

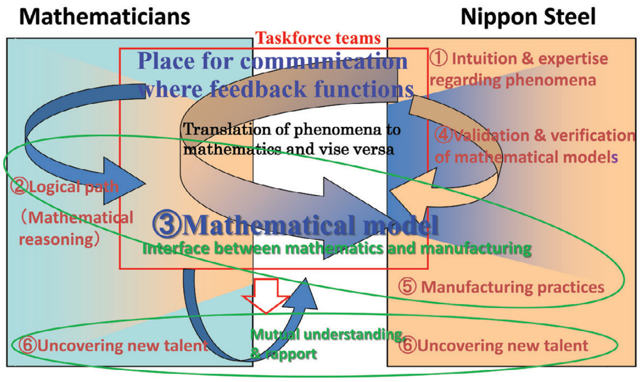


Fig.23 Collaboration style of Nippon Steel with mathematicians

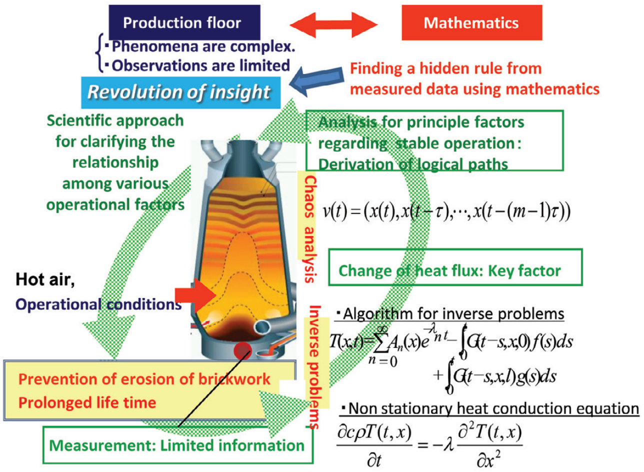


Fig.24 Concept for inverse problems of blast furnace

such phenomena inside the furnace, it became possible to quantitatively grasp the cause of an abnormal temperature change inside the furnace. Since this technology permits controlling the changes in furnace temperature, it has helped stabilize operation of the actual blast furnace.

In addition to the above inverse problem analysis, there are many techniques applying mathematics that can be used to address problems we encounter on the scene of steelmaking, such as control/optimization, data mining, visualization and pattern recognition. We consider that by implementing the expansive, bilateral industrial-academic cooperation with mathematics as its core as shown in Fig. 23, it should become possible to readily solve many of the problems encountered on the industrial scene by virtue of the universality of mathematics. In this context, we are promoting the engineering application of mathematics.

6. Conclusion

Concerning the application of mathematical science in the development of steelmaking technology, we have so far introduced examples of analyses carried out in recent years in the fields of structural analysis, fluid analysis, computational materials science and mathematics. Those examples were all multi-physical analyses embracing even heat transfer and other phenomena which are characteristic of steel. In each of the examples, a unique approach appropriate to the purpose of analysis, including relaxation of handling phenomena, was taken.

As can be seen from the examples, thanks to the rapid improvement in computer capacity, the particle discretization method which previously had only limited applications has begun to be used as a means of solving real problems. In addition, the accuracy of the analysis, which was formerly insufficient, has improved and the scale of computation has expanded markedly, making it possible to widen the sphere of analysis, focus on non-steadiness, design steel materials based on microscopic simulations, and so on. Despite the fact that the steel industry started to positively analyze its manufacturing processes earlier than any other industry, it seems that the industry has not always been able to fully benefit from the progress of high-performance computing (HPC) owing to the complexity of the objects under analysis and the difficulty involved in verification of analysis results. In the future, in order to make best use of the computer capacity that is ever increasing in scale and sophistication for our research and development, we would like to press ahead with the development of technologies for efficient parallelizing of programs and effective use of supercomputers, the development of calculation code to analyze complicated phenomena unique to steelmaking and which have not been analyzed yet, and the development of technology for the application of mathematics to expand the base of analysis.

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Kazuto YAMAMURA
Chief Researcher
Process Engineering Div.
Process Technology Center
20-1, Shintomi, Futtsu, Chiba 293-8511


Wataru YAMADA
General Manager
Mathematical Science & Technology Research Lab.
Advanced Technology Research Laboratories


Shinroku MATSUZAKI
Chief Researcher, Dr.Eng.
Ironmaking R&D Div.
Process Technology Center


Junichi NAKAGAWA
Chief Researcher
Mathematical Science & Technology Research Lab.
Advanced Technology Research Laboratories

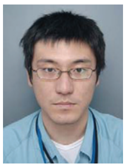

Takehiko TOH
Chief Researcher, Dr. (Environmental Science)
Mathematical Science & Technology Research Lab.
Advanced Technology Research Laboratories

Collaborator


Hideki MURAKAMI
General Manager, Ph.D.
Process Engineering Div.
Process Technology Center


Hiroshi MIO
Researcher, Dr.Eng.
Ironmaking R&D Div.
Process Technology Center


Norimasa YAMASAKI
Department Manager
Mechanical Engineering Div.
Plant Engineering and Facility Management Center


Masatomo KADOWAKI
Researcher
Ironmaking R&D Div.
Process Technology Center


Yoshihiro YAMADA
Sinior Researcher, Dr.Eng.
Mechanical Engineering Div.
Plant Engineering and Facility Management Center