Nonequilibrium dissipative structures and control over the carbon content in the spray-emulsion unit

V P Tsymbal¹, P A Sechenov¹, I A Rybenko¹ and A A Olennikov²

¹Siberian State Industrial University, 42 Kirova street, Novokuznetsk, 654007, Russia
²Tyumen State University, 15а Perekopskaya street, Tyumen, 625003, Russia

E-mail: tsymbal33@mail.ru

Abstract. The principles of creating a self-organizing spray-emulsion reactor (SER) are considered, the basis of which is the organization of forced motion of a two-phase working (reaction) mixture in the closed system under pressure, which allows a significant deviation from thermodynamic equilibrium to be created and nonequilibrium dissipative structures to be obtained. The role of dissipative structures in solving problems of controlling the chemical composition of the metal, as well as in creating a process and an unit having a small specific volume and energy capacity is shown.

1. Introduction
Studies devoted to the creation of continuous metallurgical processes especially intensively were conducted in the 70-80’s of the last century. In the collection of reports [1], entirely devoted to the development of continuous processes, units with sequentially connected baths, converter-type processes, etc., are presented. Of particular interest are studies on spray-emulsion processes, the results of which have not lost their value even today. A.M. Bigeyev, who made a great contribution to the development of the continuous steelmaking process [2, 3], considered the existence of separate chambers (zones) for the realization of the necessary technological operations (decarburization, desulfurization, dephosphorization, etc.) important and necessary along with the absence of intermediate losses of energy and raw materials. However, at that time, due to the process occurring close to the equilibrium state and, as a consequence, low rates of chemical reactions, these chambers turned out to be rather cumbersome, and the unit as a whole was capital-intensive.

In this paper it is shown that the simultaneous solution of the task of controlling the metal chemical composition and reducing the specific volume of the unit is achieved through the constructive and mode organization of dynamic dissipative structures [4], which play the role of peculiar “chambers” that were planned to be created in the initial designs of units.

2. Basic principles and solutions
The following principles and decisions were laid down in the basis of the constructive implementation of the process and unit below [4, 5]:

- organization of the forced movement of the working (reaction) mixture in the closed system under pressure, which made it possible to create a significant deviation from thermodynamic
equilibrium and simultaneously solve the problem of internal transport of reaction products through all the devices connected in series;

- creation of a large reaction surface and a two-phase working mixture (gas suspension or emulsion), that is, the conversion of the process to the gas dynamics zone, which made it possible to obtain high rates of physical and chemical processes;
- use of non-linear dependence of the flow velocity of a two-phase medium on the gas content for creating a pressure potential due to the gas-dynamic locking effect of the connecting channel;
- creation of dissipative structures that are substantially deviated from thermodynamic equilibrium, which made it possible to obtain greater control over the chemical composition of metal and slag.

Below we briefly consider these dissipative structures [4], with reference to the band model shown in figure 1: 1 – core of the compaction; 2 – reactor-oscillator; 3 – connecting channel; 4 – dynamic cushion; 5 – relatively dense gas-slag emulsion; 8 – layer of liquid metal; 6, 7 – dissipative gravitational separator.

Figure 1. Zone model of the spray-emulsion process.

1. The core of compaction on countermoving gas jets (zone 1) makes it possible to organize an intensive dispersion of the burden falling from above.

2. Reactor-oscillator (figure 2), including the said structure 1, and also zone 2 (gaseous suspension created as a result of dispersion by counter-streams) and a connecting channel 3 playing the role of gas-dynamic gate. As a result of using the effect of the nonlinear dependence of the speed of sound on gas content [6], an oscillator-reactor was created in which internal feedback is realized due to the critical outflow of a two-phase medium [4] and the influence of pressure (according to the Le Chatelier-Brown principle) on the course of chemical reactions with gas evolution, which leads to a change in the volumetric gas content in the reactor, and then to a change in the flow velocity of the two-phase medium in the connecting channel 3 by the formula:
\[
\alpha_g = \frac{v_g}{v_g + v_c}
\]

where \(v_g\) – volume of gas, \(m^3\); \(v_c\) – volume of the condensed phase, \(m^3\).

Figure 2. Reactor-oscillator: \(p_0\), \(p_f\), \(p_c\) – respectively atmospheric pressure, in the reactor and charge column; \(q_1\), \(q_2\), \(q_3\) – streams of charge, oxygen and the two-phase medium flowing out of the reactor.

Figure 3. Dependence of the sound velocity in the water-air mixture on the gas content.

The process as it were “runs” along the right branch of the nonlinear dependence of the sound velocity \(c\) on the gas content \(\alpha_g\), presented in figure 3. As a result it was possible to create a stationary oscillatory mode at any given pressure level. This is the most important link in the task of creating a self-organizing process.

3. Thus, on the basis of the oscillator-reactor, a flow stimulator (a kind of carburetor-compressor) was created, by means of which (in combination with the transfer of the process to the gas suspension and emulsion region) it was possible to create an internal transport of the working mixture through all the elements of the unit, heat recovery devices (waste heat boiler, gas turbine, fluidized bed, reformer of smoke into synthesis gas). This allows conditions for the deep use of the energy of the initial fuel to be created.

3. Dynamic “cushion”, playing the role of a failure grating (zone 4), formed as a result of the transformation of the kinetic energy of the spray emitted from the reactor-oscillator into the potential energy of pressure. This cushion separates and maintains zones 6 and 7, where mainly regenerative reactions occur, from zones 5 and 8, where oxidative reactions can occur.

4. Relatively dense gas-slag emulsion of highly foamed converter or open-hearth slag in the layer adjacent to the metal (zone 5). This zone can play a decisive role in the processes of self-organization in the refining settler, since here is the most nonequilibrium component of the process, associated with a large content of iron oxides in the slag.

5. The layer of liquid metal, zone 8 – is intended for the accumulation of metal, which is recovered in zone 6 and descending through zone 5. It should also be emphasized that oxidation reactions can occur at the boundary of zones 5 and 8, especially if relatively large pieces come to this boundary, for example, ores.

6. Dissipated gravitational separator (zone 6). This is a sufficiently high layer of foamy gas-slag-metallic emulsion suspended above zone 4, in which particles of solid oxides and carbon can also be
present. This zone occupies the overwhelming part of the column reactor (refining settler). Due to the influence of the gravitational component and the velocity of the emulsion moving close to the parabolic distribution in the cross section of the column reactor, separation of the particles takes place depending on their density. Due to this phenomenon, the particles of reduced iron, having a density two to three times greater than that of the iron oxide particles, “roll” to the periphery of the flow and form a wall layer with a negative (reverse) velocity (zone 7). This phenomenon was observed visually by us on the physical model.

It is not possible to consider the system model of the complex of dissipative structures presented above [4, 7] within the framework of this article. But it is important to note that the decomposition of the process and its model in the form of a set of dissipative structures made it possible to substantially simplify the mathematical description of this complex process. Due to the fact that self-organization takes place within each dissipative structure, or at least self-stabilization, information, in fact, folds [8], and structures are exchanged between themselves and the external environment only by the flows of matter and energy. This allows models of each dissipative cell to be built separately and the number of necessary connections between the elements (subsystems) to be significantly reduced.

Below we briefly touch on the model of only one very important structure, dissipative gravitational separator of metal, slag and gas.

Taking into account the important role of the marked dissipative structure, which connects all other zones and causes the circulation of substances in the unit, an imitation model was created for its reproduction and study [9], in which disperse particles of charge with the real specified granulometric distribution are the “first principles” – elements of the lower level of the hierarchy determined by the grain size distribution. The graphic interface of the program is shown in figures 4 a,b.
Figure 4. Fragment of implementation of the simulation model gravity separator.

The core of this model is the problem of the flow of a single particle by a vertical flow of a carrier reaction gas. With the help of a specially designed algorithm and a computer program using the Monte Carlo method, a large number of elastic and inelastic collisions of particles of charge materials and reaction products are lost, taking into account the processes taking place in them. The developed model, tested on the basis of the results of a large number of computer statistical tests coincident with the conservation laws, proved to be quite adequate “virtual reality” of the process under study). It allows the internal mechanism of complex interactions to be revealed that occur in the column reactor: to evaluate the residence time of the initial substances and reaction products, including metal and slag, in the unit; distribution of density of suspended dispersed materials along the height of the unit; influence on the course of the process of various control actions, including the granulometric composition of the metal, the ratio of ore materials to the fuel-reducing agent and other. Being a substitute object, this model allows a numerical method to solve the problems of system dynamics,
lose and develop the projected technologies. In more detail this model deserves a separate consideration [9].

3. Control of the chemical composition of metal
After getting acquainted with the basic principles of the functioning of the process and the role of dissipative structures, let us dwell on the control of the chemical composition of the metal, primarily the carbon content [10]. To do this, we again turn to the band model (figure 1). Stressing that chemical reactions occur under nonequilibrium conditions with the removal of reaction products, we note that the reactions of reducing iron oxides with solid carbon:

\[(\text{Fe}_2\text{O}_3) + C_s = 2(\text{FeO}) + \{\text{CO}\},\]  
\[(\text{FeO}) + C_s = [\text{Fe}] + \{\text{CO}\},\]  
\[C_s = [\text{C}],\]

have a preferential development in zone 6 (the top of the column reactor), and reactions with the carbon dissolved in the metal:

\[(\text{Fe}_2\text{O}_3) + [\text{C}] = 2(\text{FeO}) + \{\text{CO}\},\]  
\[(\text{FeO}) + [\text{C}] = [\text{Fe}] + \{\text{CO}\},\]

occur at the boundary of zones 5 and 8 (the turbulent layer at the metal-slag boundary) and the velocity is an order of magnitude larger than the reactions (2-4). In this case, zones 5 and 8 are separated by a dynamic “cushion” (zone 4) from zone 6.

The proportion of iron oxides processed at the slag-metal interface (zones 5 and 8) can be increased by increasing the share of larger ore materials and additional induction heating of the copier, and in zone 6, increase the recovery potential by feeding coal to the column reactor to the upper level of the gas-slag emulsion.

Thus, the possibility of creating the dynamical dissipative structures described above under certain gas dynamic modes allows us to control separately the ratio of the rates of the reducing and oxidizing processes, and, consequently, the carbon content in the resulting metal.

4. Structural and technological features of the SER unit
The use of the above described approaches and principles made it possible to create a unit with a very small specific volume and energy capacity [4, 5, 10]. The technological scheme and brief description of the SER (self-organizing spray-emulsion reactor) is presented below (figure 5). The basis of the technological scheme of the mini-module is: the charging system 1-5, the reactor-oscillator 6, the connecting channel with gas-dynamic self-locking 7, the refining settler 8, simultaneously playing the role of the first stage of wet gas scrubbing, the collector 9, and the garrison cooling system 10, the channel 11 for the delivery of a gas slag emulsion and a channel 12 for the transfer of a portion of the gas, a slag receiver 13 with a granulator 14, the system of heat recovery in the fluidized bed or the transition of flue gases into synthesis gas 17, and a gas cleaning system 18.

The high-pressure potential created in the reactor-oscillator 6, as well as the complete isolation of the process from the atmosphere, allows the products of reactions to be pushed through all the energy reclamation devices located behind the main technological unit without the use of high-temperature flow stimulators.
The dusty charge, consisting of a mixture of metal oxides and solid reducing agents, is efficiently dispersed in the reaction chamber 6. A gas suspension with a gas volume fraction of about 0.99 is produced here. Due to the dependence of the flow velocity of the two-phase medium on the gas content (Figure 3), an aerodynamically locked gate (jet braking) is formed in the connecting channel 7, and in combination with feedback on the gas content (due to changes in the conditions of chemical reactions, and oxygen) it is possible to create a stationary oscillatory mode (self-organizing reactor-oscillator).

The use of a vertical column reactor 8 as a refiner with a lower feed through the channel 7 of the reaction gas suspension combined with a significant deviation of the processes from the thermodynamic equilibrium is the most important factor that conditions the gravity separation of the iron-carbon metal stream flowing along the periphery of the column reactor and settling in the collector 9, and a stream of iron-depleted slag discharged along the inclined channel 11 to the slag receiver 13.

5. Results
When creating this unit, for the first time in world metallurgy [10] an attempt was made to use some ideas of the theory of self-organization (synergetics), such as the principles of subordination and the least coercion, a large deviation from thermodynamic equilibrium and other [11]. To realize these principles a number of physical effects was applied, such as the dispersion of the charge by counter gas jets, the creation of a self-organizing reactor-oscillator by using the critical flow of the two-phase flow and feedback on the change in the gas content of the reaction products, the lower supply of the
working mixture from the oscillator-reactor to the column reactor, the organization of forced movement and internal pneumatic transport of a two-phase working mixture.

6. Conclusion
The combination of these factors and measures made it possible to create dynamic dissipative structures in the unit, which led to a sharp decrease in the specific volume of the unit (by 10-15 times) and ensured considerable control flexibility, including the ratio of the rates of reduction and oxidation reactions, with a fairly wide range of carbon content. Currently, several dozens of new direct reduction units are being developed in the world, but in none of them, including COREX, it is possible to produce an iron-carbon alloy with a carbon content below 2%, due to the fact that the processes in them are close to the state of equilibrium and it is impossible to control separately the composition of metal and slag.

Below a comparison of technical and economic indicators of the SER process with the closest and most advanced analogue in the world – COREX unit is provided (table 1).

| Position | Indicators                  | Process COREX | Process SER | Advantage     |
|----------|-----------------------------|---------------|-------------|---------------|
| 1        | Energy intensity, GJ/t      | 29            | 15-17       | in 1.7 times  |
| 2        | Specific volume, t/m²/day.  | 1.1           | 11          | in 10 times   |
| 3        | Capital expenditures, $/t/year | 350           | 120-150     | in 2.5 times  |

References
[1] 1975 Proceedings of the meeting “Continuous processes of smelting ferrous and non-ferrous metals”, November 26 - 28, 1973, USSR Academy of Sciences, Scientific Council “Physical and Chemical Foundations of Metallurgical Processes” (Moscow: Nauka) p 204
[2] Bigeev A M 1986 Continuous Steelmaking Processes (Moscow: Metallurgy) p 136
[3] Bigeev A M 2000 Theory and Technology of Steel Melting (Magnitogorsk: MSTU) p 344
[4] Tsymbal V P, Mochalov S P, Rybenko I A et al 2014 SER Process – Metallurgical Jet-emulsion Reactor (Moscow: Metallurgizdat) p 488
[5] Tsymbal V P, Kozhemychenko V I, Rybenko I A, Padalko A G and Olennikov A A 2014 Proc. XIII Int. Cong. of Steel Makers in The Use of the Principles of Self-organization and Dissipative Structures in the Creation of a New Spray-emulsion Metallurgical Process (Moscow: Polevskoy) pp 472–477
[6] Nakoryakov V E, Pokusaev B G and Shreiber I R 1990 Wave Dynamics of Gas and Liquid – Vapour Environments (Moscow: Energoatomisdat) p 248
[7] Tsymbal V P, Sechenov P A and Olennikov A A 2016 Modeling and Knowledge-intensive Information Technologies (Novokuznetsk: SibSIU) pp 52–59
[8] Khaken G 1985 Synergetics. Hierarchy of Instability in Self-organizing Systems and Devices (Moscow: Mir) p 419
[9] Tsymbal V P, Sechenov P A, Olennikov A A and Padalko A G 2015 Proc. of the XIX Int. Sci. and Prac. Conf. in Metallurgy: Technologies, Innovations, Quality (Novokuznetsk: SibSIU) vol 1 pp 73–80
[10] Tsymbal V P, Mochalov S P and Shakirov K M 2015 Metallurgist 59 119–125
[11] Nikolis G and Prigozhin I 1979 Self-organization in Nonequilibrium Systems (Moscow: Mir) p 512