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# System-level analysis of the generation and distribution for Pb, Cu, and Ag in the process network of zinc hydrometallurgy: Implications for sustainability

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Heavy metals could serve as both pollutants and resources. To better understand the cleaner production potential of material flow control for simultaneous pollution reduction and resource conservation at source in zinc hydrometallurgy system, the generation and distribution of the Pb, Cu, and Ag in the process network of a typical zinc hydrometallurgy plant were investigated in this study. Four kinds of hazardous wastes with a total dry weight of 942 kg/tZn were identified as the major system outputs for Pb (12.08 kg/tZn), Cu (5.63 kg/tZn), and Ag (70.5 g/tZn). More than 85% of the target substances were accumulated in the leaching and purification subsystem, which determined the final proportion of the substances in the system outputs. The unsatisfactory distribution of the substances in the present process network contributes 0%, 45.9% and 27.5% of final resource wastage or pollution for Pb, Cu, and Ag of the generated wastes, corresponding to 0, 0.53 kg/tZn, and 13 g/tZn, respectively. Presently the Pb wastage or generation of Pb pollution was mainly due to the lack of recovery process. However, the potential to optimize the flow partitioning for Cu is relatively high. In summary, optimization of the process distribution might slightly increase the total recovery rate of the substances, but could significantly reduce the environmental risk of the disposed wastes generated in the zinc hydrometallurgy system. These results will be helpful to improve the understanding of the mechanisms for heavy metal pollution generation and provide further insight in the control of pollution and resource in process industries, such as nonferrous metals industry.

## 1. Introduction

The industrial application of metals continually increased during the 20th century, with around 60 metallic elements in use today (UNEP, 2011). Heavy metals produced by industrial activities is one of the most important environmental problem at present (Zhang et al., 2018). Zinc is the fourth most widely used metal after iron, aluminium and copper (Abkhoshk et al., 2014). The production of refined zinc in 2017 is up to 13 million tonnes (CNMIA, 2018), and the demand for zinc is expected to remain strong in the coming years due to the growth in the numbers of zinc consuming industries. Presently, more than 85% of the zinc metallurgy is produced by hydrometallurgical technology (NDRC, 2016). Zinc hydrometallurgy has a typical production procedure known as Roast-Leach- Electrowinning (RLE) process (Fuls and Petersen, 2011), which was hailed as an environmentally friendly alternative to zinc pyrometallurgy due to the lower energy consumption and less pollution to the atmosphere in the past. However, discharge of the solid wastes which contained heavy metals which might be far from inert is one of the most significant environmental drawbacks in the zinc hydrometallurgy industry (Anthony and Flett, 1994).

Zinc hydrometallurgy system is a highly interconnected system with many of the metals being derived from the zinc ores and as by-products. Almost all the associated metals, such as Fe, Pb, Cu, Ag, Cd, Co and Ge, imported accompanied with the raw material (*e.g.* zinc calcine) were emitted by zinc hydrometallurgy system as metabolic

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byproducts (Khosravi et al., 2018). Although the substances in the wastes were in small amount in comparison with the quantity of zinc product, considering the total production capacity of zinc, the quantity of emitted hazardous elements can not be ignored actually. It's estimated that Chinese zinc hydrometallurgy industry annually generated roughly 6,000,000 tonnes of solid wastes. Due to the high concentration of heavy metals, all the generated solid wastes were the hazardous waste according to the nation hazardous waste list (MEP, 2016), and the fate of most of them is being dumped into the landfill, causing a permanent resource wastage. The potential environmental risk is high considering their large amount of generation, posing a potential threat to the environment during the transportation and storage of the hazardous material (Wu et al., 2015). In terms of resource conservation, a certain amount of valuable metals would be discarded permanently in the landfill. For both environmental protection and resource conservation, there has been a strong demand to reduce the waste generation and resource dissipation in the zinc hydrometallurgy process to achieve sustainability.

Many efforts had been devoted to develop effective methods to recover the valuable metals from the waste of zinc hydrometallurgy system, such as recovery of Fe (Li et al., 2012), Pb (Raghavan et al., 1998), and Ag (Raghavan et al., 1998) from the leaching residue, recovery of Cu (Sethurajan et al., 2016), Co (Draganov et al., 2007), Ga (Nishihama et al., 1999) from the purification residue, and Pb from the residue from a Waelz kiln processing zinc-lead carbonate ores (Turan et al., 2004). It should be noted that most of recovery technologies applied in practice are highly selective to target substances and the properties of the residues. In general, the residues generated in different process units in zinc hydrometallurgy plant were used as different raw materials for the recovery of specific valuable metals by corresponding recovery technologies (Wang and Ma, 2008). Ma (2014) reported that resource wastage contributed by the dispersed Ag among the residues which is difficult to be reutilized would be huge. The distribution of the valuable metals in the outputs of zinc hydrometallurgy system obviously plays an important role in affecting the final recovery rate of resource. In addition, it is believed that the production activities have a big impact on distribution of heavy metal in surrounding area (Khosravi et al., 2018). Therefore, cleaner production potential might be existed in the optimization of the substance flows in zinc hydrometallurgy system, and it is necessary to understand the substance distribution of zinc hydrometallurgy system for the first step at present.

Determination of the inputs and outputs of the zinc hydrometallurgy system was frequently reported in the life cycle assessment (LCA) studies (Genderen et al., 2016; Nazari and Gharabaghi, 2015), however, extracting valuable information of the industrial co-metabolism of the associated substances from previous data was found to be difficult, since the potential impact of the emitted residues have long been neglected. In general, the existing LCA studies for zinc hydrometallurgy system focused more on the environmental effects to the atmosphere (*e.g.* the global warming potential) and water (*e.g.* marine ecotoxicity). Considering the large energy consumption and large zinc production capacity, the potential impact of the residues generation and their utilization were often excluded in the system boundary of ordinary LCA study (Nazari and Gharabaghi, 2015; Qi et al., 2017). The environmental implications of the major industrial metal (Zn) in the zinc hydrometallurgy system have been extensively studied (Guo et al., 2002; Nilsson et al., 2017; Xiao et al., 2003; Wu et al., 2015), and however, the current situation of the generation process of residues containing significant portion of hazardous (or valuable) metals, such as Pb, Ag, Cu, and Cd were rarely reported (Chen, 2004; Ma, 2014). Understanding the industrial metabolism of the material/substance is very useful for resource and environmental management of a factory, particularly for pollution prevention, source reduction and process control. For lead smelting process, Bai et al. (2015) identified and traced the material and substance destinations and quantities in the production system and determined the metabolism efficiency and the pathways through which pollutants are generated and emitted. For steel manufacturing, Yu et al. study the material and energy flows in the system (Yu et al., 2007). Given the expected increase in global future demand for Zn and their importance in today's technologies, it is important to promote the resource utilization of the wastes from zinc hydrometallurgy system in a comprehensive way, such as applying new technology, upgrading equipment in process units, and especially improving management throughout the process chain. However, in general, the zinc hydrometallurgy plant did not analysis the mass balance and distribution of the co-metabolized heavy metals (e.g. Pb, Cu, Ag, Co, Cd) and little is known about the transfer and allocation of these elements in zinc hydrometallurgy system.

Presently, implementation of environmental pollution loads control and natural resources management concerning the wastes generated in zinc hydrometallurgy system is still limited by lacking of available data. To assess the current situation of the generation and distribution of the accompanied heavy metals in the wastes of the zinc hydrometallurgy system, substance flow analysis (SFA) was employed in this study as an analytical tool for the investigation of the transfer and distribution of three valuable metals (Pb, Cu, and Pb) in the wastes of a typical zinc hydrometallurgy system. Data reconciliation technology was applied to establish the mass balance in each process unit along the process chain. A sensitivity analysis based on the transfer coefficients was carried out to quantitatively evaluate the potential influence of the flow partitioning of each process units on the fate of the target substances. The process units of the zinc hydrometallurgy system which played key role in the substance flow management for resource conservation were identified and discussed.

## 2. Method

### 2.1. Sampling and data collection

The system boundary of the present SFA study was the zinc hydrometallurgy plant encompassing all the production processes from zinc calcine leaching to zinc sheet stripping. The investigation was carried out at four individual production lines with the total production capacity of 130,000 tZn/a in a hydrometallurgical zinc enterprise in northern China. Lead (Pb), copper (Cu) and silver (Ag) were chosen as the target substances in the SFA study.

The major sources of data mainly include sampling and data collection. The total data number were over 600. The major inputs and outputs of each related process unit in the factory were sampled in fourteen regular production days. During the investigation period, there were no significant production accident and technology changes. Moisture content of the residues was measured on the day of sampling. Aqueous and solid phases were separated by 0.45 μm filter immediately after sampling. The filtrate was diluted using 0.1% $HNO_3$(Superior purity) and analyzed by Inductively Coupled Plasma Mass Spectrometry (Agilent 7500 Series ICP-MS),the power was 1200 W, sample flow rate was 0.8 ml $min^{-1}$, atomizer flow rate was 0.75 L·min-1, flow rates of carrier gas, auxiliary gas and cooling gas were 0.6 L·min-1, 0.8 L·min-1,and 13.5 L·min-1, respectively. The solid samples was firstly dissolved by 6 mL acidified (0.1 M $H_2SO_4$) solution of 5% $H_2O_2$, and digested in a closed vessel at 180 °C for 6 h. Then to remove the water and sulfuric acid of the samples by adding concentrated $HNO_3$ and 1 ml distilled water 3 times on the electric hot plate at 160 °C, respectively. Finally, all the digested samples were diluted to 50 ml with 2% $HNO_3$. and finally the heavy metal ion concentrations were also determined by ICP-MS. Considering the potential disturbance of high salinity, indium (In) and bismuth (Bi) were used as the internal standard material, and the recovery rates of In and Bi for each determination were controlled within the range of 85%–115%.

Information collection refers to obtaining the quantity of each substance flow and the available routine chemical analysis results from production reports of the enterprise. A short term of fifteen days daily reports and a long term of twelve months monthly reports were analyzed comparatively to smoothen the fluctuation of the data. The transfer volumes of the flows between processes was directly obtained from the production reports to calculated the transfer amounts of elements. Automatic dosing devices and digital flow meters applied in the production lines guaranteed the reliability and representativeness of the data. The information of raw materials consumption, zinc production, and residues output analyzed by the enterprise were used as a supplementary to the chemical analysis method for data validation and correction.

### 2.2. Establishment of the mass balance account

All the measured mass flows were normalized by the total production of electrolytic zinc products (tonnes of electrolytic zinc, tZn) and were expressed by kg/tZn. The transfer coefficient ($k$) was used to describe the partitioning of a substance in a process (Brunner and Rechberger, 2004), which was calculated from Eq. (1).

$$k_{i,p} = \frac{m_{i,p}^{\text{output}}}{\sum_i m_{i,p}^{\text{input}}} \tag{1}$$

where $k_{i,p}$ is the transfer coefficient of the output flow $i$ in the process unit $p$, and $m_{i,p}$ is the mass of the output or input flow $i$ in the process unit $p$.

The basic principle which provides constraints on the flows is that what goes into a process must come out. However, due to measurement/gross errors and process variation, mass conservation equations associated with redundant data sets are not exactly obeyed for all process (Crowe, 1996). In this study, the measured recovery rates of the substances of the outputs in majority of the process units varied from 87% to 133%. The observed recovery rates of Pb, Cu and Ag in the system were 93.81%, 131.5% and 145%, respectively. The observed unsatisfactory recovery rate of Cu and Ag might be due to the accumulated error along the process chain and that there existed concentration fluctuations of the substances (Pb: ±13.96%, Cu: ±31.93%) in the inputted raw material and the residence time of the substances in the system would be long. Therefore, prior to further interpretation of the SFA results, the inputs and outputs of the whole system need to be balanced. To overcome the inconsistencies of the data, optimally adjustment of measured data was conducted by data reconciliation technology (Pierucci et al., 1996; Shang et al., 2016; Bellec et al., 2007). For each process unit, the weighted least squares approach was applied to calculate the best fitting values which satisfied the mass balance of the substance (Brunner and Rechberger, 2004; Narasimhan and Jordache, 2000) and made the changes in their values weighted by the standard deviation, as shown in Eqs. (2)–(4).

$$\boldsymbol{X}_{\text{obs}} = (x_1, x_2, \ldots x_i)^{\mathrm{T}} \tag{2}$$

$$\boldsymbol{W} = diag\left(\frac{1}{\sigma_1}, \frac{1}{\sigma_2}, \ldots, \frac{1}{\sigma_i}\right) \tag{3}$$

$$\boldsymbol{X}_{\text{adj}} = \left((\boldsymbol{W}\cdot\boldsymbol{A})^{\mathrm{T}}\cdot\boldsymbol{W}\cdot\boldsymbol{A}\right)^{-1}\cdot(\boldsymbol{W}\cdot\boldsymbol{A})^{\mathrm{T}}\cdot\boldsymbol{W}\cdot\boldsymbol{X}_{\text{obs}} \tag{4}$$

where $\boldsymbol{X}_{obs}$ is vector containing observed mass of the flows ($x_i$) in a process unit, $\boldsymbol{W}$ is the diagonal matrix containing the standard deviation $\sigma$ of the measured mass of flow $i$, and $\boldsymbol{A}$ is the coefficient matrix providing the linear constraints.

After data reconciliation, the SFA model was then reproduced to satisfied the mass balance of the substance in the whole system based on the $k$ values of each process unit and the input flows of the system. The consistency of the data between adjacent process units in the system was achieved by an iteration method. Discrepancy between observed and estimated distribution of the substances in the system outputs was acceptable. Comparison of the observed and model estimated distribution of the substances in the system outputs is shown in Table 1.

### 2.3. Sensitivity analysis of the influence of the process unit on the system outputs

Sensitivity analysis was carried out by changing each $k$ value while leaving all others constant, and quantifying the change in model output. The central difference method was applied to evaluate the relative sensitivity based on the perturbation of the $k$ values of the process units. Although the constrain of the $k$ in a process unit was linear ($\sum k_i = 1$), the increment and decrement of the variable in the sensitivity analysis should better be taken as nonlinear considering the symmetry of the influence of the conjugated transfer coefficients. The influence of variable $k_a$ with the given increment should be equal to the influence of the conjugated variable $k_b$ with the same decrement within the range from 0 to 1 in the process unit. Therefore, a perturbation function was constructed for the calculation of the increment and decrement of $k$ in each process unit. The perturbation function is shown in Eqs. (5)–(7).

$$X_p = \{x_{i,p}\}, K_p = \left\{k_{i,p\ (i>1)}\right\}, Y_p = \left\{y_{i,\ p(i>1)}\right\} = f(X_p, \{K_p\}) \tag{5}$$

$$K_p^{t,+w\%} = \left\{\begin{array}{l} k_{i,p}\cdot(1-w\%),\ \ i\neq t \\ 1-(1-k_{i,p})\cdot(1-w\%),\ \ i=t \end{array}\right\} \tag{6}$$

$$K_p^{t,-w\%} = \left\{\begin{array}{l} (1-k_{i,p}\cdot(1-w\%))\cdot(1-k_{i,p})^{-1}\cdot k_{i,p},\ \ i\neq t \\ k_{i,p}\cdot(1-w\%),\ \ i=t \end{array}\right\} \tag{7}$$

where $X_p$ and $Y_p$ represent the mass flow of the inputs and outputs in the process unit $p$, respectively. $K_p$ represents the transfer

**Table 1**
Comparison of the estimated and observed substance distribution in the system outputs.

| Output | Pb |  | Cu |  | Ag |  |
|---|---|---|---|---|---|---|
|  | Observed | Estimated | Observed | Estimated | Observed | Estimated |
| RP1 | 7.07% | 5.94% | 83.19% | 75.60% | 4.45% | 10.11% |
| RP2 | 2.43% | 1.99% | 8.11% | 13.93% | 0.31% | 1.08% |
| RA | 89.27% | 90.13% | 8.56% | 9.86% | 89.68% | 82.12% |
| RI | 1.24% | 1.94% | 0.14% | 0.62% | 5.56% | 6.70% |

coefficients of the process unit $p$. The $f(X_p, K_p)$ is the transfer function of the substance flow in a process unit. The $w$ is the preset increment/decrement degree ($w$=10). The $K_p^{t,+w\%}$ and $K_p^{t,\text{-}w\%}$ are the calculated transfer coefficient vectors with perturbation, and the gaps between $K_p^{t,+w\%}$ and $K_p^{t,\text{-}w\%}$ would equal to a constant $\Delta k$ value of 10% (0.1). The influence of the $k$ of the process unit on the process outputs could be evaluated by Eqs. (8) and (9).

$$IF_{p,i}^{t,+} = \sum_t \frac{\partial Y}{\partial K_p^{t,+w\%} \bullet y_i} = \sum_{\mathrm{t}} \frac{f\left(X, \left\{K_p^{t,+w\%}\right\}\right)_i - f(X,K)_i}{f(X,K)_i} \tag{8}$$

$$IF_{p,i}^{t,-} = \sum_t \frac{\partial Y}{\partial K^{t,-w\%} \bullet y_i} = \sum_{\mathrm{t}} \frac{f\left(X, K^{t,-w\%}\right)_i - f(X,K)_i}{f(X,K)_i} \tag{9}$$

$$IF_{p,i} = \left| \frac{IF_{p,i}^{+} - IF_{p,i}^{-}}{2} \right| \tag{10}$$

where $IF_{p,i}^{t,+}$ and $IF_{p,i}^{t,\text{-}}$ are the relative sensitivity of the $k_t$ with the increment and decrement, respectively, on the process output $i$ in the process unit $p$. It should be noted that the influences of increasing and decreasing $k$ values on the outputs are different (*e.g.* with a value of the transfer coefficient close to 1, the influence of further increasing the partitioning ratio of the substance flow would be little). Since the process units in the system have the process outputs no more than two and $IF_{p,i}^{a,+}$ equals to $IF_{p,i}^{b,\text{-}}$ when $k_a$ and $k_b$ were conjugated ($k_a$+$k_b$ = 1), therefore, the $IF_{p,i}$ in Eq. (9) was used to evaluate the synthesized influence of the flow partitioning of the process unit $p$ on the process output $i$. Then the influence on the process outputs was integrated into the topological structure of system, and finally was propagated to the system outputs. An iteration method was employed to resolve the complete mass unbalance of the whole system induced by the modification of $k$ values in a process unit. The influence of the flow partitioning of the process unit on the process outputs could be further extrapolated to that on the final system outputs, and were named as $IFS^+$, $IFS^-$ and $IFS$ which corresponds to $IF^+$, $IF^-$ and $IF$, respectively.

## 3. Results and discussion

### 3.1. Process units and substance flows related to the waste generation

In the zinc hydrometallurgy system under study, 20 process units and 44 strands of substance flows were identified and examined in total, as shown in Fig. 1a. The zinc hydrometallurgy system could be divided into four subsystems, mainly including leaching, purification, feeding, and electrolysis. It was found that more than 90% of the Pb, Cu, and Ag flux was accumulated in the subsystems of leaching and purification, as shown in Fig. 2. The generation of anode slime in electrolysis process could be viewed as the input sources (labeled as E-M in Fig. 2) of Pb and Ag. Therefore, for the investigation of Pb, Cu and Ag in the zinc hydrometallurgy system, the system boundary of the SFA study could be adjusted to focus more on the core process units. The sketched substance flow chart based upon the lead and copper related flow data and the process units is shown in Fig. 1b. The name and description of each process unit, and the mass and the $k$ value of each flow can be found in Table 2.

In the simplified zinc hydrometallurgy system, 22 strands of substance flows were used to represent the flow of Pb and Cu and Ag. There were 12 major process units worked together to produce qualified electrolyte for electrolysis. Since the selectivity of leaching zinc from the zinc calcine is relatively low, a multi-stage purification (P1 and P2) was used to further purify the electrolyte. The main production objective of the rest process units is to make the most use of the zinc in zinc calcine. It could be found that although many substance flows and process units in the zinc hydrometallurgy system were clipped, the simplified system is still complex.

### 3.2. Potential of the system to concentrate/dilute the substance

To make the structure of the system clear, the optimal vertex order (finding the minimum feedback vertex set (Lin and Jou, 2000)) was employed to illustrate the directed graph which was abstracted from the process network, as shown in Fig. 3. It is clear that 8 process units in the system had more than 2 outputs, which determined the fate of the end of the substance in the system. The number of the arc in the minimum feedback arc set was determined to be 2, which means that when the 2 feedback arcs were removed from the graph, a directed acyclic graph would be obtained. Therefore, the number of feedback arcs could be viewed as the number of the circulation flows in the system. The process units in the system which could interact with each other through the 2 circulation flows, showing that the exchange of the substances between process units is extensive. In addition, the whole process chain could be split into 13 stages, which would be used for the estimation of the changes of relative statistical entropy (RSE).

The moisture contents and the dry weight of the outputs and the concentration of the Pb, Cu and Ag are shown in Table 3. The generation ratio of the dry weight of the sum of the four solid wastes to the produced zinc is 0.942, which means that in the production of every one tonne of electrolytic zinc, there was nearly one tonne of solid hazardous wastes generated in the zinc hydrometallurgy system. The RA accounted for 61.6% of the weights of the total wastes, and followed by RI (25.8%), RP2 (6.9%) and RP1 (5.5%). The fate of most of the residues was entering into the hazardous waste landfill.

In comparison with the substance concentration in the zinc calcine(#O-L), Pb was enriched in RP1 (2.9 times) and RA (4.18 times), and Cu was enriched in RP1 (26.3 times) and RP2 (3.83 times), and Ag was enriched in RP1 (4 times) and RA (3.5 times). This showed the potential of substance recovering for both resource conservation and environmental protection. In the zinc hydrometallurgy plant under study, around 89% of the Cu in the RPs (RP1 and RP2) was recovered as cathode copper through the comprehensive utilization process by electrodeposition method. RA was separately used as the raw material for the recovery of Ag (recovery rate: 68%). No additional recovery process was found for Pb.

Control of the waste material flows in the zinc hydrometallurgy system would be similar to the case of waste and resource management in modern incineration system (Rechberger and Brunner, 2002; Brunner and Rechberger, 2004), which both aim at concentrating the hazardous or valuable substances into highly enriched residues for better environmental management or resource reutilization. In this study, the potential of the zinc hydrometallurgy system to concentrate or dilute Pb, Cu, and Ag was quantified using the statistical entropy analysis method (Brunner and Rechberger, 2004). For comparison purpose, in this case, we calculate the RSE of the elements in aqueous and solid phase seperately and estimated the contribution of them equally. When the target substance serves both resource and pollutant, dilution is believed to be an important reason to worsen the system performance (Bai et al., 2015; Luo et al., 2018; Rechberger and Brunner, 2002). The reference concentrations for calculating the RSE of aqueous phase were taken from the electrolyte and that in solid phase were taken from the zinc calcine for better evaluation of the decrease of resource potential of the elements.

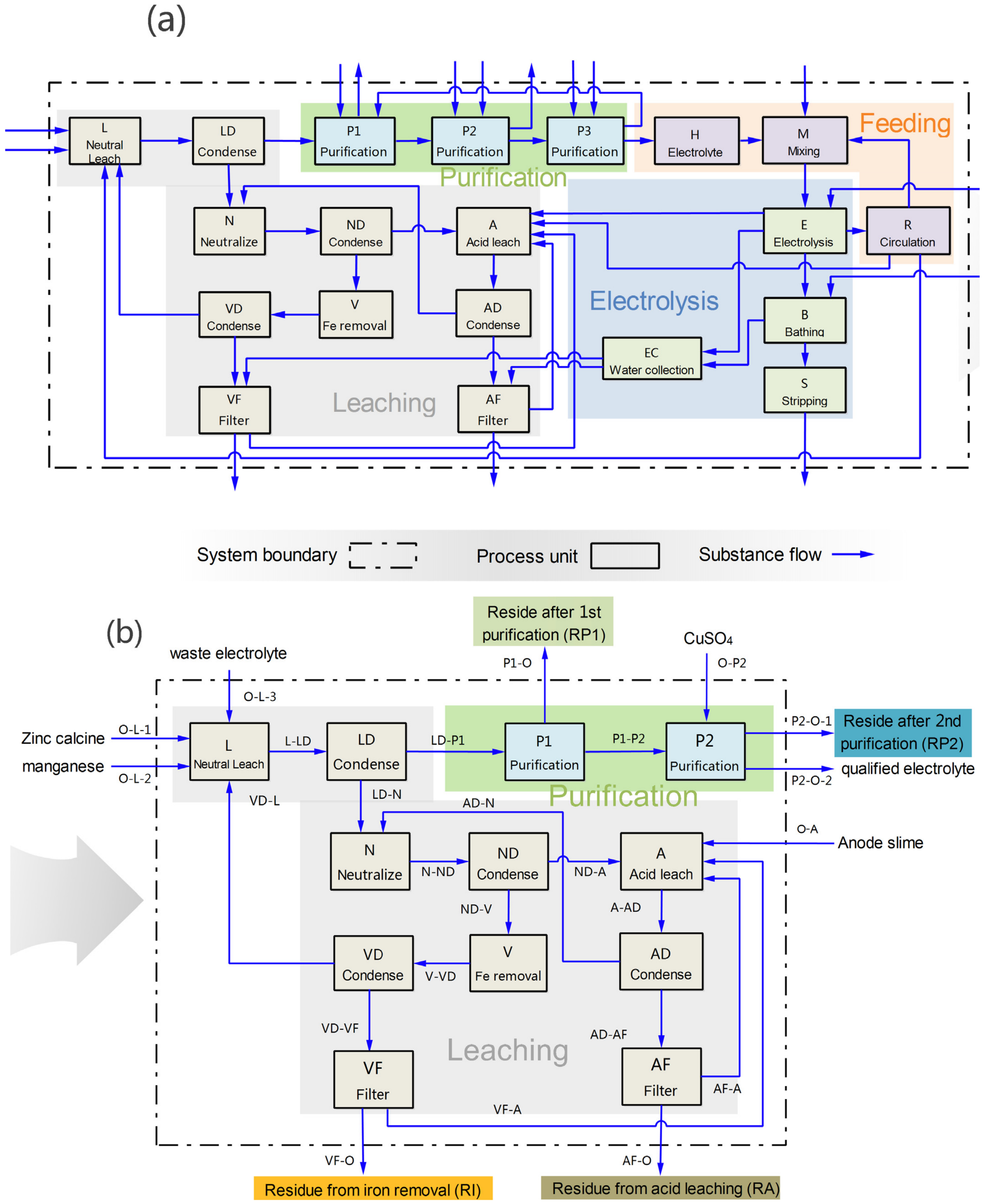

**Fig. 1.** Substance flow chart of zinc hydrometallurgy system based on the process units related to Pb, Cu and Ag transfer (a: typical zinc hydrometallurgy system; b: the simplified system after boundary adjustment).

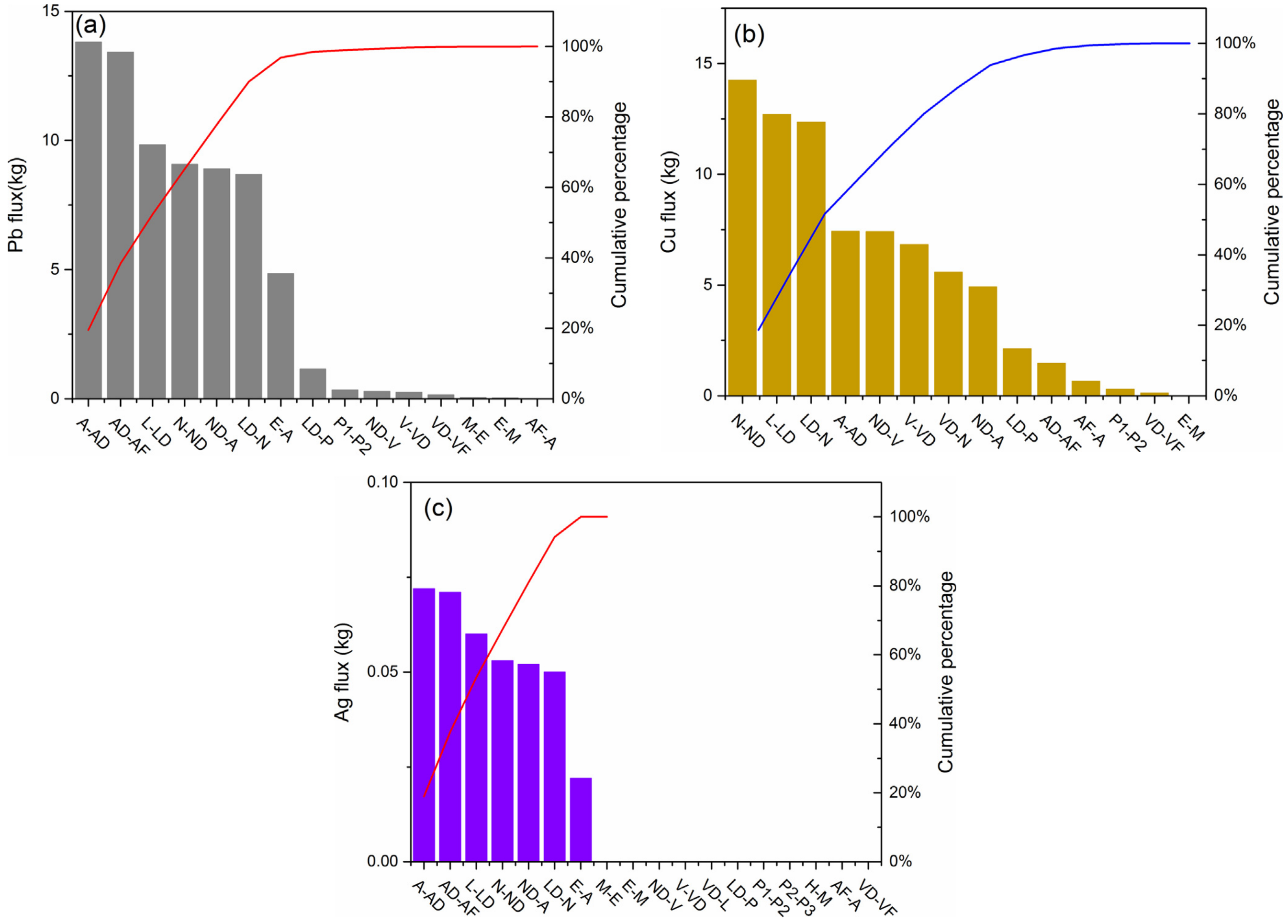

**Fig. 2.** Flux distribution of the substance in the process units (a: Pb, b: Cu, and c: Ag).

**Table 2**
Description of the main process units and the mass (kg/tZn) of the substance flows containing Pb and Cu in the zinc hydrometallurgy process.

| Process unit | | Output of the process unit[a] | | Pb | Cu | Ag |
|---|---|---|---|---|---|---|
| L | Neutral leaching | #L-LD | Ore pulp | 9.838 | 12.352 | 0.062 |
| LD | Thickening | #LD-P1 | Supernatant of ore pulp | 1.151 | 4.920 | 0.008 |
| | | #LD-N | Concentrated ore pulp | 8.687 | 7.422 | 0.053 |
| P1 | Purification of electrolyte | #P1-RP1 | Residue generated in 1st purification | 0.854 | 4.266 | 0.007 |
| | | #P1-P2 | Electrolyte after 1st purification | 0.266 | 0.629 | 0.001 |
| P2 | Purification of electrolyte | #P2-RP2 | Residue generated in 2nd purification | 0.294 | 0.786 | 0.001 |
| N | Neutralization | #N-ND | Mixed ore pule | 9.005 | 12.711 | 0.055 |
| ND | Thickening | #ND-A | Concentrated mixed ore pulp | 8.833 | 5.582 | 0.050 |
| | | #ND-V | Supernatant of the ore pulp | 0.173 | 7.129 | 0.006 |
| A | Acid leaching | #A-AD | Ore pulp | 11.143 | 7.413 | 0.061 |
| AD | Thickening | #AD-N | Supernatant of the ore pulp | 0.318 | 5.289 | 0.002 |
| | | #AD-AF | Concentrated ore pulp | 10.825 | 2.124 | 0.059 |
| AF | Solid-liquid separation | #AF-A | Ore pulp after filtration | 0.041 | 1.568 | 0.001 |
| | | #AF-RA | Residue generated in filtration | 10.784 | 0.556 | 0.058 |
| V | Deironing | #V-VD | Reacted ore pulp | 0.173 | 7.129 | 0.005 |
| VD | Thickening | #VD-VF | Concentrated ore pulp | 0.150 | 0.299 | 0.005 |
| | | #VD-L | Supernatant of the ore pulp | 0.022 | 6.831 | 0.0001 |
| VF | Solid-liquid separation | #VF-A | Ore pulp after filtration | 0.001 | 0.264 | 0.0001 |
| | | #VF-RI | Residue generated in filtration | 0.149 | 0.035 | 0.005 |
| O [c] | Outside of system boundary | #O-A | Anode slime | 2.262 | - | 0.010 |
| O [c] | Outside of system boundary | #O-L | Zinc calcine | 9.814 | 5.520 | 0.061 |
| O [c] | Outside of system boundary | #O-P2 | Copper sulfate additive | - | 0.122 | - |

[a] The names of the material flow followed the format: “#upstream process unit”-“downstream process unit”.

[c] The “O” means the outside of system boundary.

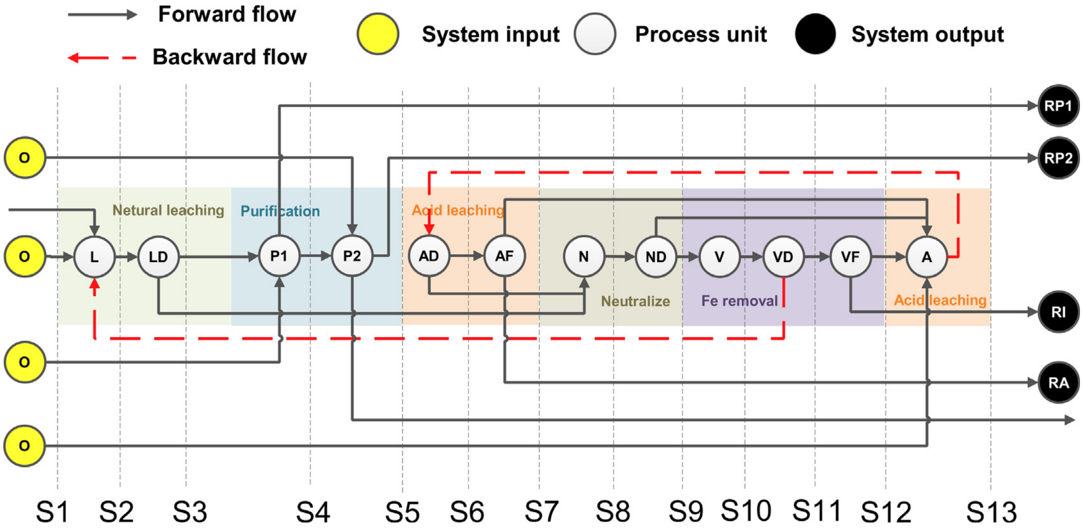

**Fig. 3.** Optimal vertex order of the directed graph abstracted from the process network.

**Table 3**
The dry weight and percentage ratio of the substance content of the inputs and outputs of the system.

| Substance flow | Dry weight (kg/tZn) | Moisture content | Concentration of the substances (*w*/*w*) | | |
|---|---|---|---|---|---|
| | | | Pb | Cu | Ag |
| *Inputs* | | | | | |
| #O-L | 1780.7 | - | 0.55% | 0.31% | 0.0034% |
| #O-A | 31.6 | 30% | 7.17% | - | 0.0317% |
| #O-P2 | 0.66 | - | <0.01% | 24.2% | - |
| *Outputs* | | | | | |
| #P1-RP1 | 52.3 | 32.74% | 1.5% | 12.5% | 0.0137% |
| #P2-RP2 | 65.4 | 26.52% | 0.42% | 1.8% | 0.0011% |
| #AF-RA | 580.4 | 27.45% | 2.1% | 0.10% | 0.0282% |
| #VF-RI | 243.7 | 26.84% | 0.07% | 0.01% | 0.0044% |

Calculation of the relative statistical entropy (RSE) based on the concentration and quantity of the substance was employed to evaluate the potential of the system to concentrate/dilute the inputs into outputs in each stage, as shown in Fig. 4. Smaller RSE indicated relatively larger enrichment degree of target elements under this condition. It can be seen that Pb and Ag had similar characteristics of enrichment and transfer. Those two elements were firstly enriched during the initial leaching process of S1-S2 and then diluted in the following acidic leaching process, which were reflected in the variation trends of RSE. In the whole stage, the RSE contribution of Pb and Ag in liquid phase was always low, indicating that solid phase was the main metabolic form of Pb and Ag, and the RSE change of Pb and Ag was mainly affected by element content in the residues. However, Cu presented opposite variation trends than Pb and Ag, it was diluted during S1-S2 stages and then enriched in subsequent residue forming processes. The analysis of RSE contribution in liquid phase showed that Cu was firstly leached and dispersed in liquid phase (the proportion of liquid phase increased), and then gradually concentrated to solid phase. Therefore, preventing the dilution of Pb and Ag in the acid leaching process or the dilution of Cu in the leaching was important for a better concentration of the elements in the residues of the present zinc hydrometallurgy system. However, it should be noted that the increase of the substance concentration efficiency of the system did not mean that the substance would enter into their favored ends which benefits subsequent resource recovery and pollution management.

### *3.3. Mass balance study on the waste generation and resource dissipation*

The mass balance result showed zinc calcine (#O-L) is the major source of the substances, accounting for 67.0% (9.811 kg/tZn), 97.9% (5.521 kg/tZn) and 73.7% (0.0603 kg/tZn) of the total inputs of Pb, Cu and Ag, respectively. The Pb and Ag in the anode slime generated from the corrosion of lead based anode in the zinc electrowinning process is the second important input source of Pb (#O-A), accounting for the rest of system inputs, respectively. The use of $CuSO_4$ as the additive to purify the impurities of the electrolyte in P2 is the second source of Cu of the system. Since the quantities of Pb, Cu and Ag included in the produced zinc sheet (the product of the zinc hydrometallurgy system) were negligible, the lifecycle of Pb, Cu and Ag in the system could be completely viewed as the industrial metabolism of the waste from the beginning when they were introduced into the system. After being transferred along the process chain, the inputted Pb and Cu were mainly distributed into the four major system outputs (RP1, RP2, RA, RI). The total distribution ratios of Pb, Cu and Ag into the four system outputs can be found in Table 1.

The schematic view of the full mass balance of the substances in the system in combination with the recovery process is shown in Fig. 5. It was found that although the process recovery rates for Cu and Ag were 89% and 68%, the total recovery rate for them were only 79.6% and 57.5%, respectively. The dissipation of Cu and Ag could be mainly attributed to two parts that the unsatisfactory

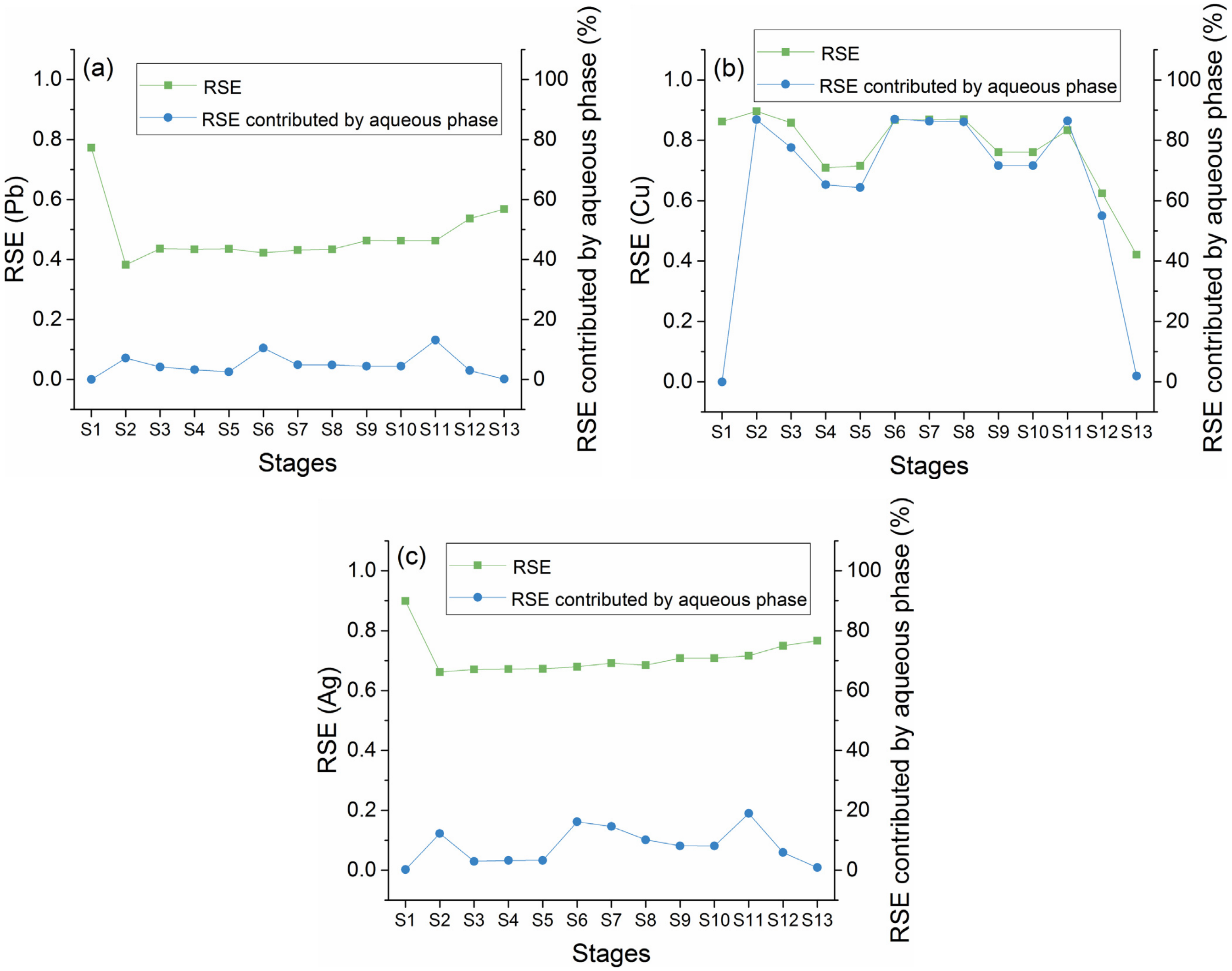

**Fig. 4.** Change of the relative statistical entropy between system in each stage (a: Pb, b:Cu, c:Ag).

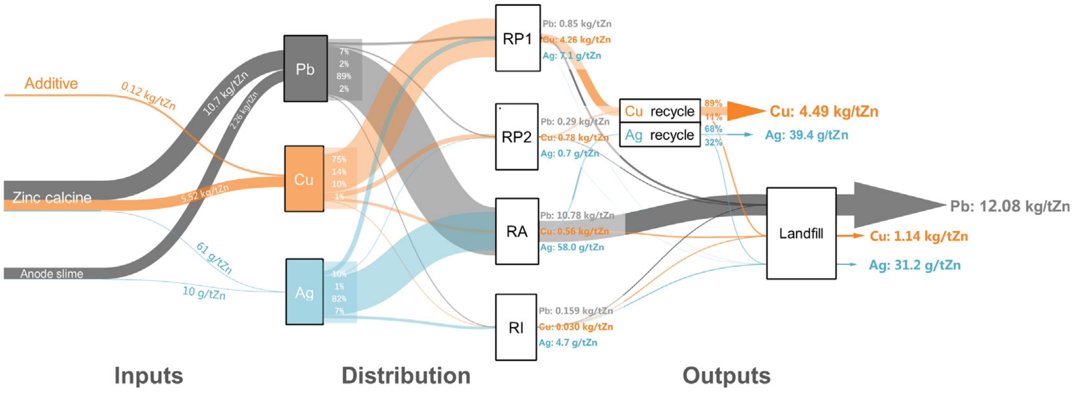

**Fig. 5.** Schematic view of the mass balance of the substances in the zinc hydrometallurgy system.

substance distribution caused by the system, and the technical limitation in their corresponding subsequent recovery process. The contribution of these two parts can be quantitatively estimated based on Eq. (11).

$$C_i = \frac{NRF_i \times r_i}{NRF_i + RF_i \times (1 - r_i)} \times 100\% \tag{11}$$

where $C_i$ is the contribution of the unsatisfactory distribution to the resource wastage or pollution generation for substance $i$, the contribution of low recovery rate in the subsequent recovery process is given by $(1\text{-}C_i)$, $NRF_\mathrm{i}$ is the amount of substance $i$ which did not enter into the subsequent recovery process, $RF_\mathrm{i}$ is the amount of substance $i$ which entered into the subsequent recovery process, and $r_\mathrm{i}$ is the recovery rate of the subsequent recovery process for substance $i$. More attentions should be given to the substance distribution if the contribution is significant. Especially when the subsequent recovery rate is high, the substance distribution in the system plays important role in the resource and pollution management. It was found that the $C_{\mathrm{Pb}}$, $C_{\mathrm{Cu}}$, and $C_{\mathrm{Ag}}$ were 0%, 45.88% (NRF: 0.53 kg/tZn), and 27.53% (NRF: 13 g/tZn), respectively. For Cu, the optimization of Cu distribution in the outputs is required most for pollution control and resource management. For Ag, the resource wastage or pollution generation is mainly contributed by the low recovery rate in the subsequent recovery process. However, for Pb, the addition of resource recovery process is expected more rather than just optimizing the substance distribution.

### 3.4. *Evaluation of the influence of process units on the substance distribution in the outputs*

There were more than 80% of Pb and Ag distributed into RA, and around 75% of Cu entered into RP1, indicating that the present zinc hydrometallurgy system has a strong selective tendency of allocating different substances. Before the process optimization was carried out, it is important to understand and evaluate the potential and influence of each process unit in the process chain on the substance distribution in the final system outputs. To investigate the distribution behavior of the substances in the system, the influence of the flow partitioning in each process unit on the substance distribution in the detailed system outputs were quantitatively estimated based on the IFS values through the sensitivity analysis. The detailed proportion changes of the substances contributed by each process unit on each system outputs (indicated by IFS) were drawn in the heat maps, as shown in Fig. 6. The heat maps of the influences of process units on system outputs for Pb and Ag have similar pattern (Fig. 6(a and c)), indicating that the transfer behaviors these two substances in the processes of zin hydrometallurgy system were highly correlated (r = 0.932), and should be managed together. This is because that Pb and Ag are easy to form sulfuric acid insoluble salt, and most of them are transferred along with the solid phase, which is dominated by the thickening process. LD, P1 and ND were the key process units which have significant potential influence on the distribution of Pb and Ag in the current system.

In comparison with Pb and Ag, the sulfuric acid salt of Cu is soluble and thus the heat maps of the influences of process units on system outputs for Cu showed a different pattern, as shown in Fig. 6b. Most of these process units (except for P1) contributed equally to concentrating Cu into RPs, with the IFs between 0−0.022. This showed that most of the process units had the potential to further increase total Cu recovery rate in the present system. P1 and VF have the smallest influence on the recovery of Cu in the system, since that for P1, the Cu partitioning determines only the ratio of Cu in RP1 and RP2 (which will both enter the Cu recovery process), and for VF, the quantity of the inputted mass flow of Cu is small and the influence of the Cu partitioning changing in VF on the Cu distribution might be neutralized by the subsequent circulations in the system.

The perturbation function used for $k$ in the sensitivity analysis indicated that further increase or decrease the partition ratio of the flows would be limited by the existing large (close to 1) or small (close to 0) $k$ values in the process unit. To better explore the bottlenecks of the process units on the resource conservation in the system outputs, the influences of the $k$ value in the process unit with increment (IFS$^+$) and decrement (IFS$^-$) were investigated independently, as shown in Fig. 7 (RA± or RPs± represent the increase or decrease of the target substances in their expected system output(*i.e.* RA or RPs)). It was found that the thickening behavior of LD and ND played the most important role in concentrating Ag and Pb into the expected output (RA). However, in comparison with other three outputs, the potential of the system to further increase the enrichment of Ag and Pb in RA was low. This is because that the selectivity of the system is already high enough for the transfer of Pb and Ag from system inputs to RA, and most of the transfer coefficients for Pb and Ag in the major transfer path to RA are over 0.9. However, as shown in the blue columns from Fig. 7(a and c), although the corresponding increase of the substances enrichment in RA is not significant, optimization of (VD, VF and ND) and LD showed the significant potential to reduce the Pb and Ag contents in RI and RPs, respectively. AF seemed to have almost no influence on the distribution of Pb and Ag in the system, since different outputs of AF would be still gathered into same system outputs finally (*e.g.* RA).

For the resource conservation of Cu, we need to increase the substance enrichment in RPs to facilitate the effective recovery of Cu. As shown in the blue columns of Fig. 7b, LD, ND, AD and AF has the relatively large potential to increase Cu proportion in RPs. LD is the most important process unit which should be responsible for Cu lost in the present zinc hydrometallurgy system. In most of the process units, the Cu enrichment in RPs were negatively correlated with that in RA, indicating that entering into RA was the primary way of causing Cu loss. In addition, it was found VD and VF had significant influences on decreasing the content of Pb, Ag, and Cu in RI. Therefore, individual optimization of VF (reducing the proportion of transferred Cu into RI) and VD (reducing the ratio of transferred Cu into VF) or adding extra process unit to change the flow directions of Cu would be a feasible way to selectively reduce the environmental risks of RI brought by Cu.

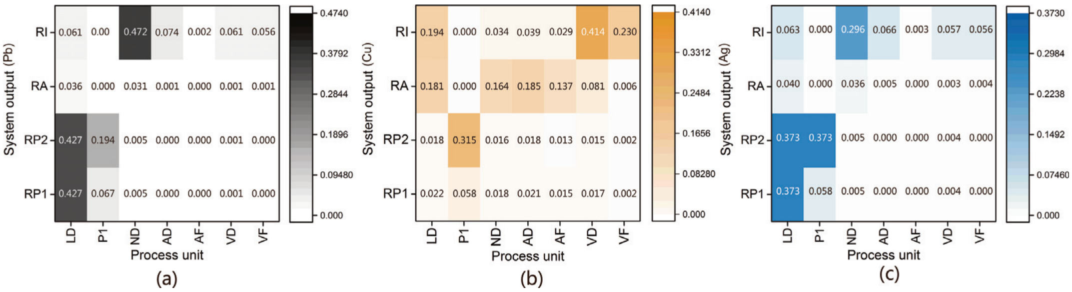

**Fig. 6.** The heat maps of influences of the process units on the substances variation in the outputs (a: Pb, b:Cu, c:Ag).

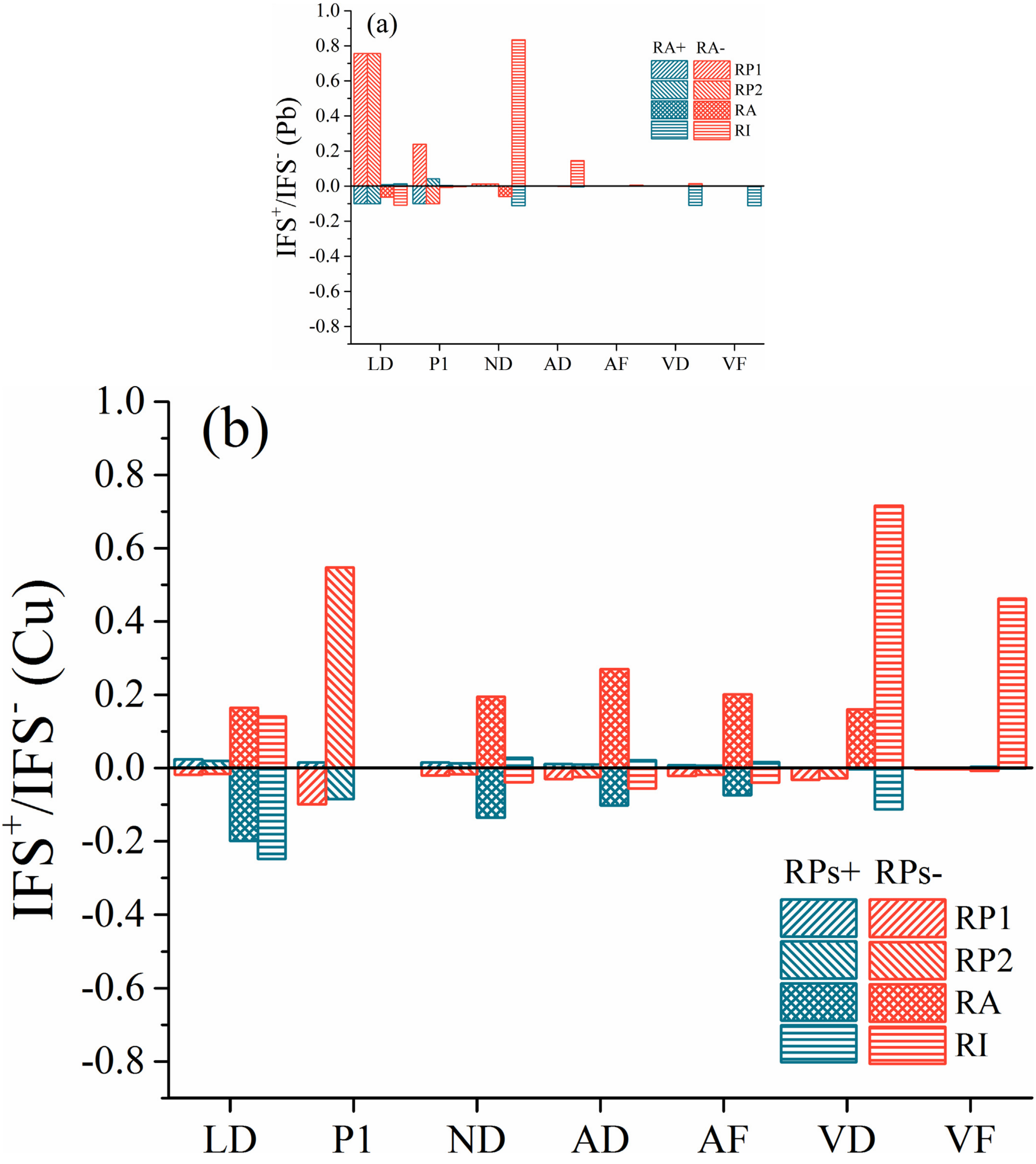

**Fig. 7.** The influences of the *k* value with increment (IF$^+$) and decrement (IF$^-$) in the process unit on system outputs (a: Pb, b: Cu, c: Ag).

## 4. Conclusions

Substance flow control is important for simultaneous pollution reduction and resource conservation in zinc hydrometallurgy system especially for the heavy metals which could serve as both pollutants and resources. In this study, cleaner production potential was found existed in the generation and distribution of Pb, Cu and Ag in the process network of zinc hydrometallurgy system. The

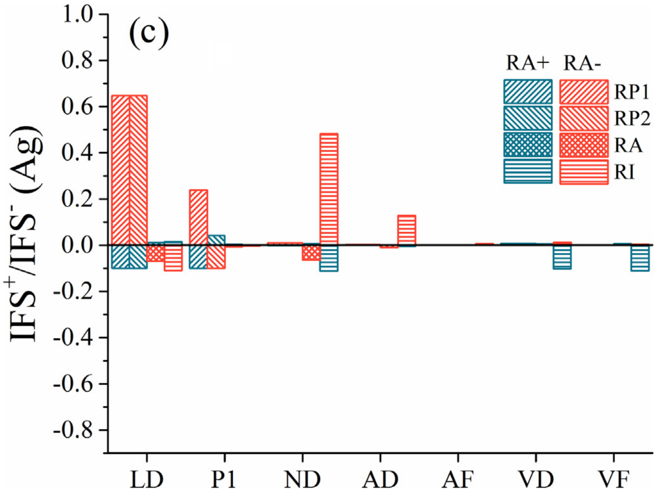

**Fig. 7.** (*continued*).

unsatisfactory distribution of the substances in the present process network contributes 0%, 45.9% and 27.5% total resource wastage or pollution generation of Pb, Cu and Ag of the generated wastes, corresponding to 0, 0.53 kg/tZn, and 13 g/tZn, respectively. The distribution of the substances were mainly determined by the leaching and purification subsystems, which accumulated 90% of the total substance fluxes. In the present zinc hydrometallurgy system, Pb and Ag showed similar distribution patterns in the process network, and should be managed together. For Cu, the potential to increase the final resource conservation and reduce total pollution generation by optimizing the flow partition existed in many of the process units (e.g. LD, ND, AD, and AF). Optimization of the process distribution would increase the total recovery rate of the substances slightly, but has the potential to significantly reduce the environmental risk of the disposed wastes generated in the zinc hydrometallurgy system. When the influence and opportunity were evaluated and identified, optimization of the substance distribution in the system needed to be considered as one of the most important process prevention options for producing less harmful substances and reducing the dissipation of natural resource to achieve sustainability.

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